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ACTA POLYTECHNICA SCANDINAVICA

CHEMICAL TECHNOLOGY SERIES No. 282

Lactic Acid Based Poly(ester-urethane) - Modification via Copolymerization, Chain Linking and Blending

JANNE KYLMÄ

Helsinki University of Technology
Department of Chemical Technology
Polymer Technology
P.O. Box 6100
FIN-02015 HUT, Finland

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Chemical Technology for public examination and debate in Auditorium KE 2 (Komppa Auditorium) at Helsinki University of Technology (Espoo, Finland) on the 11th of May, 2001, at 12 noon.

ESPOO 2001

Kylmä, Janne, **Lactic Acid Based Poly(ester-urethane) - Modification via Copolymerization, Chain Linking and Blending.** Acta Polytechnica Scandinavica, Chemical Technology Series No. 282, Espoo 2001, 47 pp. Published by the Finnish Academies of Technology, ISBN 951-666-570-5, ISSN 1239-0518.

Keywords: Biodegradable polymers, Poly(ester-urethane), Lactic acid, Polycondensation, Copolymerization, Chain extending, Blending, Impact-modification

ABSTRACT

The properties of biodegradable lactic acid based poly(ester-urethanes), PEU, were chemically and physically modified and the structure-property relationships investigated. The heat resistance of PEU was improved by copolymerization of lactic acid with DL-mandelic acid. The glass transition temperature of poly(L-lactic acid-co-DL-mandelic acid-urethanes) showed a marked increase with increased mandelic acid composition. Molecular weight depression was attributed to the steric hindrance of the bulky phenyl group of mandelic acid. Novel biodegradable and thermoplastic poly(ester-urethane) elastomers were synthesized by the copolymerization of lactic acid and ε-caprolactone. Properties, such as glass transition temperature and mechanical properties were strongly dependent on the composition of the copolymer. Small amounts of ε-caprolactone increased the strain of PEU, and at higher caprolactone content the poly(L-lactic acid-co-ε-caprolactone-urethane), P(LA/CL)U, exhibited elastomeric properties, having lower strength but significant elongation.

The rheological properties of PEU were enhanced by modification of the structure of the polymer chains. An increase in the amount of 1,6-hexamethylene diisocyanate (HMDI) as a chain extender caused branching, which was revealed by the broadened MWD and increased shear thinning at low frequencies. The chain linking technology for lactic acid prepolymers was further developed with the use of highly effective carboxyl and hydroxyl reactive chain extenders. Reaction between 2,2'-bis(2-oxazoline) (BOX) and the carboxyl groups of the lactic acid oligomer led to a hydroxyl terminated prepolymer with low acid value, which provided a significant increase in molecular weight in the HMDI linking reaction. The introduction of oxamide groups into the polymer structure increased the chain stiffness, which was detected in enhanced mechanical properties and an increase in the glass transition temperature.

The impact strength of poly(ester-urethane) was significantly improved by blending. The toughening was achieved with a finely dispersed P(LA/CL)U or copoly(L-lactide/ε-caprolactone) elastomer phase in the matrix PEU. Tensile modulus and strength showed a downward trend as a function of rubber content but remained at an acceptable level. Good compatibility and interactions at the rubber-matrix interface were observed. The relationship between phase separation and mechanical properties of rubber-toughened blends was investigated. Composition of the elastomer, i.e. ε-caprolactone content, was found to determine the formation of the heterophase structure. The degree of crosslinking in the P(LA/CL)U rubber was another important factor in the impact modification. Furthermore, the balance between impact strength and stiffness of the poly(ester-urethane) composites was considerably improved by the addition of particulate or fibrous fillers as a third component.

PREFACE

This work was carried out at Helsinki University of Technology, Laboratory of Polymer Technology between January 1995 and December 2000. The research was part of the National Technology Agency (TEKES) "Biodegradable Polymers Technology Programme 1992-1996" and targeted research projects thereafter. These projects were focused on the polymerization and properties of lactic acid based polymers for bulk applications, i.e., large-scale utilization of biodegradable and compostable polymers derived from renewable resources.

I wish to express my gratitude to Professor Jukka Seppälä for his advice, continued interest and for providing me with the opportunity to work at his laboratory. I gratefully acknowledge my co-workers Jukka Tuominen, Mari Hiljanen, Antti Helminen, Kari Hiltunen, and Mika Härkönen for their contribution, valuable comments, and collective hard work. Warm thanks are extended to Jaana Rich and Teija Karjalainen for thoughtful comments, valuable help and discussions in many areas. A large number of colleagues and friends have positively contributed to this work.

The personnel of the laboratory are thanked for creating a positive and pleasant working atmosphere and especially for their guidance and all the help during the research. In particular, I would like to thank Jorma T. Hakala for his enthusiastic literature research. Eija Ahonen and Arto Mäkinen are sincerely thanked for technical assistance, as are all the students and trainees who helped over these years.

I am thankful to Jyrki Juhanoja for the scanning electron micrographs and the Electron Microscopy Unit of the Institute of Biotechnology, University of Helsinki, for providing laboratory facilities. Kathleen Ahonen and Anton Rich are thanked for revising the language of the publications and this thesis.

Co-operation with industry has brought different perspectives to this research - Johan-Fredrik Selin (Fortum), Soili Peltonen (VTT Chemical Technology), Hannu Suksi (Metsä-Serla), and Merja Itävaara (VTT Biotechnology) are thanked. The financial support received from the National Technology Agency (Tekes) is gratefully acknowledged.

I wish to thank my parents for steady support over the years. To my wife Anna Kaisa my deepest gratitude for her love and support during this work.

Helsinki, February 2001

Janne Kylmä

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LIST OF PUBLICATIONS

This thesis is based on the following seven publications (Appendices I -VII), which are, throughout the overview, referred to by their Roman numerals.

I Kylmä, J., Härkönen, M., and Seppälä, J. V., The Modification of Lactic Acid Based Poly(ester-urethane) by copolymerization, *J. Appl. Polym. Sci.* **63** (1997) 1865-1872.

II Kylmä, J. and Seppälä, J. V., Synthesis and Characterization of a Biodegradable Thermoplastic Poly(ester-urethane) Elastomer, *Macromolecules* **30** (1997) 2876-2882.

III Hiljanen-Vainio, M., Kylmä, J., Hiltunen, K., and Seppälä, J. V., Impact Modification of Lactic Acid Based Poly(ester-urethanes) by Blending, *J. Appl. Polym. Sci.* **63** (1997) 1335-1343.

IV Kylmä, J., Hiljanen-Vainio, M., and Seppälä, J. V., Miscibility, Morphology and Mechanical Properties of Rubber Modified Biodegradable Poly(ester-urethanes), *J. Appl. Polym. Sci.* **76** (2000) 1074-1084.

V Kylmä, J. and Seppälä, J. V., Ternary Phase Poly(ester-urethane)/Elastomer/Filler Composites, *J. Appl. Polym. Sci.* **79** (2001) 1531-1539.

VI Helminen, A., Kylmä, J., Tuominen, J., and Seppälä, J. V., Effect of Structure Modification on Rheological Properties of Biodegradable Poly(ester-urethane), *Polym. Eng. Sci.* **40** (2000) 1655-1662.

VII Kylmä, J., Tuominen, J., Helminen, A., and Seppälä, J., Chain Extending of Lactic Acid Oligomers. Effect of 2,2'-Bis(2-oxazoline) on 1,6-Hexamethylene Diisocyanate Linking Reaction, *Polymer* **42** (2001) 3333-3343.

The author's contribution in the appended publications

Publications I, II, and V: Janne Kylmä is responsible for the research plan, experimental work, interpretation of the results, and the preparation of the manuscript.

Publications III and IV: Janne Kylmä and Mari Hiljanen are jointly responsible for the research plan, experimental work, interpretation of the results, and the preparation of the manuscript.

Publication VII: Janne Kylmä and Jukka Tuominen are jointly responsible for the research plan, experimental work, interpretation of the results, and the preparation of the manuscript. Rheological measurements and interpretation of these results were carried out by Antti Helminen.

Publication VI: Janne Kylmä has participated in the preparation of the research plan and interpretation of the results, and has contributed to the preparation of the final version of the manuscript.

NOMENCLATURE

AV	acid value, acid number
BD	1,4-butanediol
BOX	2,2'-bis(2-oxazoline)
CAA	citric acid anhydrous
CL	ɡ-caprolactone
DLMA	DL-mandelic acid
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
E0%	lactic acid oligomer, 0 mol% BD
FTIR	fourier transform infrared spectroscopy
GA	glycolide
HBA	4-hydroxybenzoic acid
HMDI	1,6-hexamethylene diisocyanate
LA	lactic acid
LLA	L-lactic acid
L-LA	L-lactide
DLLA	DL-lactic acid
MLA	DL-malic acid
NMR	nuclear magnetic resonance spectroscopy
NOE	nuclear Overhauser effect
OX	oxazoline end-group
PDLA	poly(D-lactide) or poly(D-lactic acid)
PDLLA	poly(DL-lactide) or poly(DL-lactic acid)
PEU	poly(ester-urethane)
PLA	poly(lactic acid) in general regardless of the polymerization method
P(LA/CL)U	poly(L-lactic acid-co-ε-caprolactone-urethane)
P(L-LA/CL)	copolymer of L-lactide and ε-caprolactone
PLLA	poly(L-lactide) or poly(L-lactic acid)
SEC	size exclusion chromatography
SEM	scanning electron microscopy
$Sn(Oct)_2$	tin(II) ethylhexanoate

SYMBOLS

E'	storage modulus (Pa)
E"	loss modulus (Pa)
eta*	complex viscosity (Pa⇳s)
G'	storage modulus (Pa)
G"	loss modulus (Pa)
L/D	aspect ratio, length/diameter
M_n	number average molecular weight (g/mol)
M_w	weight average molecular weight (g/mol)
MWD	molecular weight distribution
tan δ	damping factor, E"/E'
T_g	glass transition temperature (°C)
T_m	melting temperature (°C)

1 INTRODUCTION

1.1 General background

The field of biodegradable polymers is a fast growing area of polymer science because in the interest of such polymers for temporary surgical and pharmacological applications.[1] On the other hand, biopolymers offer a possible alternative to traditional non-biodegradable polymers in a number of bulk applications if recycling is impractical or uneconomical. Composting, which is used for the disposal of food and yard waste, is the most suitable for the disposal of biodegradable materials together with food contaminated paper.[2] In addition, non-degradable polymer products are generally produced from nonrenewable resources such as crude oil and natural gas, while a combination of biodegrability and the application of annually renewable sources offers the chance to make plastics part of a natural cycle.[3]

Polymers of lactic acid belong to a group of aliphatic polyesters, which are the most readily biodegradable thermoplastic materials. Lactic acid (2-hydroxy propionic acid) can be manufactured either by microbial fermentation of biomass or chemical synthesis, although fermentation predominates and thus the criterion of renewable raw material is fulfilled. Figure 1 depicts the polymerization methods which are currently available for poly(lactic acid) (PLA) synthesis. Lactic acid is a hydroxy acid, having both a hydroxyl and a carboxyl group, which enables it to be polymerized directly via a polycondensation reaction into polyester. This polycondensation is, however, an equilibrium reaction, which is not easy to drive to completion because of the difficulty of removing water from the very viscous melt and the simultaneous formation of the lactide. Polycondensation produces low molecular weight oligomers, which are unusable for many applications unless external linking agents are used to increase the molecular weight of the polymer. High molecular weight PLA has also been obtained in an azeotropic polycondensation where the water is removed from the reactor as an azeotropic mixture with the solvent, such as diphenyl ether, under reduced pressure.[4,5] Lactic acid polymers are most commonly prepared by ring-opening polymerization of lactide, i.e., cyclic diester of lactic acid. Under rather mild conditions, high molecular weight polyesters can be prepared in a short period of time. Lactide monomers used for ring-opening polymerization are generally obtained by the depolymerization of lactic acid oligomers.[6]

The presence of asymmetric carbon atoms generates structural particularities, which make lactic acid-derived polymers rather special when compared with other polymers.[7] Lactic acid possesses one asymmetric carbon and exists in two configurations, referred to as L- and D-lactic acid. Thus, lactic acid cyclic dimers exist as either L-lactide, D-lactide, or the *meso* form which has both L and D configuration on the same dimer molecule. An equimolar ratio of L- and D-lactic acid or L- and D-lactide is referred to as racemic DL-lactic acid or DL-lactide, respectively. The thermal, mechanical, and biodegradation properties of lactic acid polymers are known to depend on the choice and distribution of stereoisomers within the polymer chains. High-purity L- and D-lactides form stereoregular isotactic poly(L-lactide) (PLLA) and poly(D-lactide)(PDLA), respectively. These are semicrystalline polymers with a high melting point ($T_m \sim 180°C$) and a glass

transition temperature in the 55-60°C range. The degree of crystallinity depends on many factors, such as molecular weight, thermal and processing history, and the temperature and time of annealing treatments. The *meso*- and DL-lactide, on the other hand, form atactic poly(DL-lactide) (PDLLA) which does not crystallize, i.e., is amorphous.[8] The mechanical properties and degradation kinetics of the semicrystalline PLLA are quite different from those of completely amorphous PDLLA. In particular, PLLA is always preferred whenever higher mechanical strength and longer degradation time are required.[9] Basically, lactic acid polyesters have the characteristics of a stiff, glassy material.

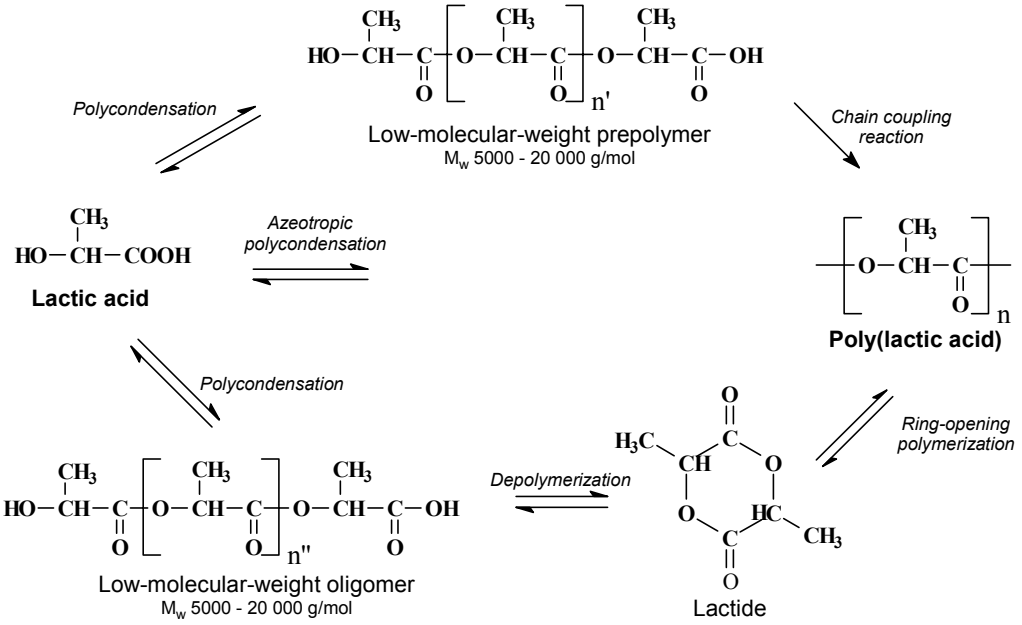

Figure 1. Polymerization methods to poly(lactic acid).

1.2 Modification of lactic acid polymers - a literature review

The chemical and phase structures are the major determinants of the properties of biodegradable polymers.[10] These structures, and thereby the chemical and physical properties of lactic acid based polymers, can be adjusted through changes in polymerization and processing conditions; by copolymerization and variation of the copolymer composition as well as through other chemical modification; by blending with other polymers, and by compounding with additives, such as fillers, plasticizers, dyes, and stabilizers. These methods of modification applied to PLA polymers are discussed in this section.

Polymerization

Polycondensation of lactic acid is usually performed in bulk by distillation of condensation water, with or without catalyst, while vacuum and temperature are progressively increased. Although, as

stated above, high molecular weight polyesters with good physical properties are not easy to obtain, the properties of lactic acid oligomers, which can be further used as intermediates in the synthesis of polyurethanes, can be controlled by the use of different catalysts and functionalization agents, and by varying the polymerization conditions.[11,12]

Ring-opening polymerization of lactide can be carried out in melt, bulk, or in solution and by cationic, anionic, and coordination-insertion mechanisms depending on the catalyst.[6,13,14] The choice of initiator system, co-initiators as chain control agents, catalyst concentration, monomer-to-initiator ratio, and polymerization temperature and time significantly affect the material properties. These properties, such as the molecular weight, degree of crystallinity and residual monomer content, in turn affect the physical-mechanical properties and temperature use range of the polylactides and its copolymers.[7,15,16,17,18,19,20] The role of the racemization and the extent of transesterification in the polymerization and copolymerization process are also decisive for the enantiomeric purity and chain microstructure of the resulting polymer.[21,22,23,24] Many current PLA polymerization methods employ stannous octoate as the catalyst, since it has been shown to be very effective, causes a low degree of racemization at high temperature,[25] has low toxicity, and is accepted by the US Food and Drug Administration.[26]

Copolymerization

Copolymerization of lactic acid or lactide with other monomers has been recognized as a valuable tool in modifying the properties of the homopolymers. Although PLA polymers appear very versatile, in general the properties of homopolymers can only be slightly modified by varying the molecular weight or crystallinity, and copolymers are required to provide materials with a wider range of properties. The PLA copolymers can present all the classical structures, namely random, diblock or multiblock, star, etc., with all the consequent variations in properties one can predict from such differences.[7]

Only a few monomers have been shown to increase the glass transition temperature (T_g) of poly(lactic acids). Fukuzaki and co-workers[27,28,29] have used α-hydroxy acids containing aromatic rings as the side groups or in the main chains to stiffen the oligomer chain. L-lactic acid was copolycondensed with aromatic hydroxy acids such as p-hydroxybenzoic acid, p-hydroxy-phenylacetic acid, and p-3-(hydroxyphenyl)propionic acid, or monomers having aromatic rings as side-group residues, e.g. DL-mandelic acid and L-3-phenyllactic acid (!C_6H_5, !CH_2!C_6H_5). In lactide copolymerizations, the incorporation of glycine and salicylic acid repeating units has increased the T_g.[30,31,32]

Another approach is to lower T_g and improve low temperature properties by increasing the flexibility of PLA. Copolymers of lactide and glycolide (GA) have found wide-spread use as biomedical materials due to increased hydrophilicity and enhanced degradation.[33,34] In all copolymerizations of L-lactic acid or L-lactide the length of crystallizable LA sequences is greatly reduced as compared with homopolymerizations, it can therefore be expected that, as the amount of comonomer increases, the crystallinity and the melting temperature of the copolymer will be reduced. The L-LA/GA copolymers in the composition range 25-65 wt.% GA are fully amorphous. Similarly, in stereocopolymers of L-lactide and D- or DL-lactide, the melting temperatures of the

semicrystalline copolymers decrease as the content of D-units increases.[35] This random incorporation of a small amount of lactide enantiomer of opposite configuration has been utilized in varying the degradation profile, but it has also been the most widely used method for improving PLA processability.[36,37,38] Copolymers of lactide and ε-caprolactone (CL) have a wide variety of mechanical properties, ranging from elastomeric to rigid, depending on the composition and the average sequence length.[39,40,41] The chemical microstructure of these copolymers varies from random to diblock arrangement, depending on the polymerization and the type of initiator used. Transesterification, i.e., the exchange reaction of ester groups between different chains, generates the redistribution of sequences in the polyester chain, thus changing its microstructure.[42] Lactic acid derivatives,[43] other lactone[44,45,46] and ether lactone[47,48] monomers, as well as trimethylene carbonate[49,50,51] and its dimethyl derivatives[52] have also been widely studied as comonomers to obtain copolymers with versatile properties.

Modifications to the degradation kinetics of PLA, especially in drug release systems, have been of interest. The incorporation of flexible water soluble polyethers, such as poly(ethylene glycol) and poly(propylene glycol) or their respective monomers, to form random and block copolymers, enables variation of hydrophilicity, biodegradation rate, and of course the final mechanical properties.[53,54,55,56] In addition, poly(orthoester) and poly(anhydride) have been reported as bioerodible materials, and thus the PLA copolymers with corresponding monomers have shown surface erosion behavior.[57,58]

On introduction of functional side groups by copolymerization, variation in the physical properties can be achieved. PLA copolymers with pendant side-chain amino groups of the lysine[59,60,61] and di-hydroxyl[62] groups will provide a functional handle to attach bioactive molecules and to prepare graft copolymers. The free carboxylic acid groups, obtained from the copolymerization of malic acid,[63,64] can also be further functionalized to manipulate the material properties. These groups are thought to have a catalytic effect on the hydrolytic scission of the ester bonds, increasing the degradation rate. Copolymers with polydepsipeptides having pendant carboxyl and amino, or thiol groups have also been reported.[65] In addition, Chen et al.[66] have copolymerized a cyclic carbonate monomer, which has a cyclohexene group, with L-lactide to introduce C=C functional groups. This provides opportunities to introduce other functionalities or free radical crosslinking.

Crosslinking

The crosslinking of homo- and copolymers of linear polylactones would provide further possibilities for modifying the physical and mechanical properties of these materials. According to Nijenhuis et al.[67], a tetrafunctional monomer, 5,5'-bis(oxepane-2-one), is an excellent lactone crosslinker for improving the impact and tensile strengths. Spiro-bis-dimethylene-carbonate has been used in the crosslinking of poly(lactide) chains to influence thermal properties, without necessarily leading to deterioration in the mechanical properties.[68] Peroxide crosslinking with dicumyl peroxide proved to be effective in the crosslinking of PLLA. The crosslinking resulted in a ductile material.[67]

Chain linking of lactic acid oligomers

Chain coupling of low molecular weight oligomers is not only an alternative route for synthesizing PLA polymers, but it also offers the possibility of introducing different functional groups into the polymer chain. Improved mechanical properties and flexibility in the manufacture of copolymers are also associated with the use of chain extending agents. Typical extenders for polyesters that contain -OH and -COOH groups are diisocyanates, diepoxides, bisoxazolines, dianhydrides, and bisketeneacetals.[69,70] Polyurethanes are a unique class of polymers, with a broad range of properties which can be tailored by varying the type and amount of their components. Linear poly(ester-urethanes) have been synthesized by reacting either lactic acid or lactide based polyol with different diisocyanates.[71,72,73] In poly(D,L-lactide-urethane) networks, the physical properties were further enhanced with increasing crosslinking density. This was attributed to a higher degree of hydrogen bonding provided by the urethane segments.[74] The chemical make-up of the polyester polyol enabled the design of physical properties in lactide and ε-caprolactone based polyurethanes.[75,76]

A poly(ester-amide) structure was presented by Tuominen and Seppälä[77], where polycondensed carboxyl terminated lactic acid prepolymers were chain extended with 2,2'-bis(2-oxazoline). The mechanical properties appeared to be slightly better than for the corresponding urethanes.

Polymer-polymer blends

Chemical modification is not the only method for changing the properties of the polymer. In many cases, this can be performed more rapidly and cost-effectively by mixing available polymers using existing processing equipment rather than through the development of new chemistry. The final properties of these blends depend on the chemical structure of the original components, the mixing ratio of the constituent polymers, the interaction between the components, and the processing steps to which they are then subjected. In polymer-polymer blends of PLA, the primary problem has been to find polymers that exhibit at least some degree of miscibility or compatibility. Most of the blends were found to be immiscible, including a phase-separated morphology, and yielding blends with poor mechanical properties. In addition, the second component must also be biodegradable, which make the process less economically attractive in some cases. However, several blend systems containing PLA have been investigated, such as blends of PLA with poly(ε-caprolactone),[78,79,80] poly[(R)-3-hydroxybutyrate],[81,82,83] poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate],[84] poly(ethylene oxide),[85,86,87] and poly(vinyl acetate).[88]

An interesting phenomena in blends of poly(L-lactide) and poly(D-lactide) is the formation of a stereocomplex. The PLA stereocomplex is found to possess a racemic crystalline structure, where PDLA and PLLA chains are packed side by side with a D monomer unit to L monomer unit ratio of 1:1. One of the most interesting findings in PLLA/PDLA stereocomplexation studies is that the melting temperature of the stereocomplex is 230°C, approximately 50°C above that of the corresponding homopolymer. This enantiomeric polymer blend also exhibits substantially higher tensile properties and better thermal stability and hydrolysis resistance than the polylactides from which the blends are prepared.[89,90]

Rubber toughening

In general, semi-crystalline and amorphous poly(lactic acid) is a relatively brittle polymer with low impact resistance. One successful route for improving the impact resistance of polymers is rubber toughening. In this process, rubber modification is achieved by phase separation in the blend, when typically between 3 and 20 wt.% rubber is incorporated as a dispersed phase into a continuous matrix phase. Phase separation between hard and flexible components is important because a rubber that is miscible with the matrix acts as a plasticizer. Secondly, the adhesion between the phases at the rubber-matrix interface is an important parameter in rubber toughening, and therefore the rubber is ideally neither completely compatible nor completely incompatible. The resulting blends show significant improvements in impact strength, elongation at break, work to break, and fracture toughness, with only slight reductions in modulus and tensile strength. Factors affecting rubber modification include the chain structure of the matrix; phase separation and interfacial adhesion of matrix and rubber; particle size, shape, volume fraction, and type of rubber.[91,92]

Grijpma and co-workers[93,94,95,96] have studied the rubber toughening of poly(L-lactide) and amorphous non-crystallizable lactide stereocopolymers with several hydrolytically degradable rubbers. Rubber modification with poly(trimethylene carbonate), poly(trimethylene carbonate/ε-caprolactone), or poly(L-lactide/ε-caprolactone) rubbers resulted in increased impact strengths, lower yield strengths, and higher elongations. Randal et al.[97] have prepared poly(lactide) composites with improved impact resistance, using epoxidized natural rubber elastomer as a second phase. In order to improve compatibility of the phases they have used a reactive compatibilizing agent. In addition, Sinclair and Preston[98] have used non-biodegradable rubber in rubber toughened poly(lactide) blends.

Fillers and Plasticizers

Fillers are usually solid additives mixed with plastics to improve material properties, to introduce specific characteristics, or to reduce the cost of the compound. In the case of mass volume biodegradable polymers, cost reduction has practical importance beside improvement in the mechanical properties. Fillers are inorganic or organic materials, and each group consists of fibrous and nonfibrous types. Individual fillers are available in a number of grades differing in average particle size and size distribution, particle shape and porosity, chemical nature of the surface, and impurities. As a result of the presence of filler, hardness and stiffness are increased while impact and tensile strengths are usually decreased.[99,100,101] Thakur et al.[102] have found that talc, which is commonly added as a filler, also acts as a nucleating agent for poly(lactide) and increases the number of spherulites in crystallization. Kolstad[38] concluded that 6 wt.% talc gives a 500-fold increase in the nucleation density. Hiljanen-Vainio et al.[103] have recently enhanced the mechanical properties of lactic acid based poly(ester-urethane) via the addition of organic and inorganic fillers.

Primarily, plasticizers are added to polymers to achieve flexibility and processability, although many other properties are also modified. Typically, when plasticizers, such as citrate esters, poly(ethylene glycol), glucosemonoesters, and fatty acid esters, have been used with poly(lactic acid), the increase in plasticizer content has caused a corresponding reduction in modulus, tensile strength, and softening temperature, whereas elongation at break and toughness have been

improved.[104,105] Poly(lactic acids) are also plasticized with their own monomers and oligomers.[106,107] The use of a plasticizer such as lactide or lactic acid is beneficial in producing more flexible materials, but due to the fast migration of the rather small molecules, it results in unevenness in films and sticking during processing.[103,108] Sinclair and Preston[109] have also used unreacted monomer and oligomers for impact modification of poly(lactide).

Processing

Poly(lactic acids) are thermoplastics that can readily be processed by conventional means, including extrusion, injection molding, and film blowing. One major disadvantage of PLA is that it belongs to the group of polymers which are relatively sensitive to thermal degradation. Molecular weight decrease under processing conditions has an extensive effect on the properties of the final products.[110] Postulated thermal degradation reactions in poly(lactide) are intramolecular transesterification from the end of the chain (back-biting) or in the middle of the chain, intermolecular transesterification, hydrolysis, and pyrolytic elimination.[111] The parameters that have been reported to influence thermal stability include molecular weight, end-groups, moisture, residual or hydrolyzed monomers and oligomers, impurities, and residual metals.[112,113,114,115,116,117] Since the degradation rate under processing conditions is strongly dependent on the nature and amount of metal catalyst used, the thermal stability of polylactides is remarkably enhanced when the ring-opening polymerization is initiated by aluminium isopropoxide rather than stannous octoate.[118] In addition to this, obvious methods for the removal of any organometallic compound are solvent extraction or solvating and selective precipitation of the polyester.[119,120] Industrially, the more reasonable and straightforward strategy is the post-polymerization quenching of the metal catalyst by deactivating agents, including various types of peroxides,[121,122,123] boron compounds,[124] tropolone,[125] and phosphite-containing or phenolic compounds.[108] These compounds are supposed to deactivate the catalyst and to decrease its activity in transesterification reactions. However, the use of a free-radical promoter, such as benzoyl peroxide, tends to induce chain branching and cross-linking reactions.[118] Acetylation of end-groups has also led to an increase in thermal stability.[114]

The intrinsic properties of PLA polymers have also been modified for a specific application by processing techniques. Törmälä et al.[126,127,128] have introduced the self-reinforcing technique, where poly(L-lactic acid) rods are reinforced with highly oriented fibres of the same polymers, achieving higher strength materials for fixation devices in orthopedic applications. In addition, high strength fibres for general medical applications have been prepared using melt or solution spinning processes, which involve orientation of the chains by cold- and/or hot-drawing.[129,130,131] PLA films can be draw-oriented up to about 8 times before showing strain whitening, but considerable enhancement of properties can be achieved with nominal draws of 3 to 5 times.[132]

1.3 Scope of the study

The polymerization of lactic acid polymers, based on a two-step process depicted in Figure 2, has been developed and extensively studied in our laboratory at Helsinki University of Technology. The process involves condensation polymerization of lactic acid to low molecular weight hydroxyl-terminated prepolymer, where 1,4-butanediol is used for hydroxyl termination. In the second step, these telechelic prepolymers are linked with diisocyanate, typically 1,6-hexamethylene diisocyanate (HMDI), to high molecular weight poly(ester-urethane) (PEU). PEU is an amorphous, thermoplastic polymer, which has been shown to be biodegradable.[133,134] It has the characteristics of a glassy material that resists high stresses but has no capacity for deformation (i.e., hard-brittle material). The flexibility in the selection of reactants has been utilized in our previous studies. Hiltunen and co-workers[11,12] have condensation polymerized prepolymers having different molecular weights with various catalysts, diols, and their combinations, whereas Tuominen and Seppälä[77] have chain linked carboxyl terminated lactic acid prepolymers with 2,2'-bis(2-oxazoline).

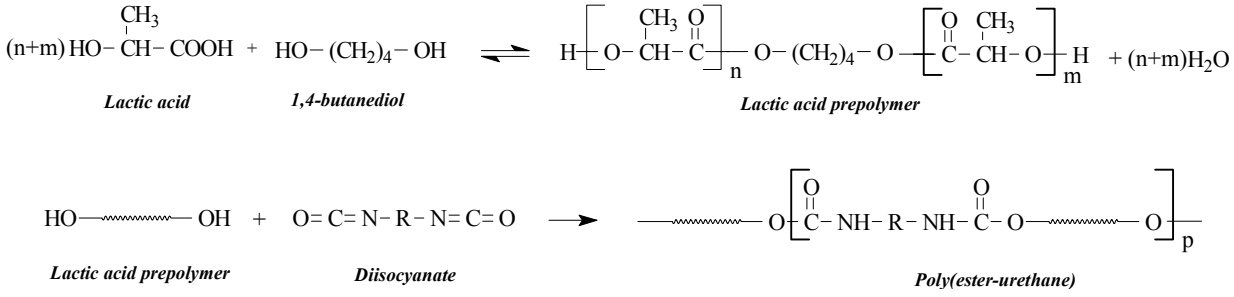

Figure 2. Polymerization scheme of lactic acid based poly(ester-urethane).

This thesis discusses the research reported in seven appended publications (I-VII). The primary goal of the research was to improve specific properties and investigate the structure-property relationship of chemically and physically modified lactic acid based poly(ester-urethanes). The first part of the work, papers I and II, concern the modification of lactic acid prepolymers by copolymerization, which further affects the properties of PEU. Firstly, attention was focused on improving heat resistance, i.e., increasing the glass transition of the PEU, by incorporating rigid groups in the polymer chain. Secondly, the aim of the research described in publication II was to synthesize a series of novel thermoplastic poly(ester-urethane) elastomers based on copolymers of L-lactic acid and ε-caprolactone.

In publications VI and VII, attention was turned to the chain linking of lactic acid prepolymers. The rheological properties of PEU were modified by adjusting the amount of chain extender. Secondly, to avoid problems associated with the polycondensation of hydroxyl terminated prepolymers and to introduce new characteristics into the polymer chain, 2,2'-bis(2-oxazoline) was used as end-group modifier and chain coupling agent in the prepolymers before actual chain linking with diisocyanate. The effects of bis(2-oxazoline) on the carboxyl end-group content of the

prepolymers, the progress of the diisocyanate reactions, and the properties of the obtained polymers were investigated.

The final part of the work, publications III-V, involved the physical modification of poly(ester-urethane). The objective was to design and prepare a series of PEU blends where the multiphase nature of the system would afford the required versatility in mechanical properties. The primary interest was to increase the impact resistance of PEU by blending a small amount of rubber as a dispersed phase into a rigid matrix. The miscibility of the blends, dispersion of the rubber phase, and mechanical and thermal properties of the blends were characterized. The ternary phase polymer composites containing both rubber-modifier and rigid filler were investigated with the aim of achieving an optimum balance of toughness and stiffness.

2 EXPERIMENTAL

2.1 Materials

The L- and DL-lactic acid (Fluka or ADM: Archer Daniels Midland Co.) used was initially 88% lactic acid in water and was purified by distillation under vacuum. 1,4-Butanediol (Fluka or Acros Organics) and stannous octoate (tin(II) ethylhexanoate, Sigma or Aldrich) were used as received, as well as all comonomers, ε-caprolactone (Fluka), DL-mandelic acid (Fluka), 4-hydroxybenzoic acid (Fluka), 4-acetoxybenzoic acid, DL-malic acid (Fluka), and citric acid anhydrous (Fluka). 1,6-Hexamethylene diisocyanate (Fluka), isophorone diisocyanate (3-isocyanatemethyl-3,5,5-trimethyl-cyclohexyl-isocyanate; Hüls), and 2,2'-bis(2-oxazoline) (Tokyo Kasei) were used as the linking agents.

Three different wollastonite fillers were used: Wicroll 10 PA surface-treated with aminosilane (aspect ratio (L:D) 8:1), untreated Wicroll 10 (L:D 8:1), and FW 325 (aspect ratio 3:1), all from Partek Nordkalk. The other silicate filler, Aktisil PF 224 (Hoffmann Mineral), a natural mixture of corpuscular quartz and lamellar kaolinite, was stearyl amine coated. Talc (Finntalc M20SL; Finnminerals) was of particle size <20 μm. Organic fibre-like materials investigated were wood fibre (Solka Floc cellulose fibre, particle size 40-165 μm) and flax. The flax fibre and the other fibrous reinforcement glass fibre (Ahlstöm Glassfibre) were cut on average to 10 mm length.

2.2 Polymerization

A general two-step route for poly(ester-urethane) polymerization is presented in Figure 2 on page 14. The prepolymers were prepared by condensation polymerization in a rotation evaporator or in a bench scale reactor. In primary screening, test tube polymerization was used. L-lactic acid, and in publication II also DL-lactic acid, was polymerized together with 0-4 mol% 1,4-butanediol, which was added to produce hydroxyl-terminated oligomers. Stannous octoate, $Sn(Oct)_2$, was used

as a catalyst. In copolymerizations, the comonomers were added in the specified mole proportions. The reaction mixture was polymerized at 200-210°C for 24 h, with a continuous nitrogen flow fed under the surface of the melt, and at a reduced pressure.

The linking polymerizations of the prepolymers were carried out in several reactors, which were capable of agitating viscous materials: a designed glass reactor, a bench scale reactor equipped with twin spiral agitator (KK Juchheim GmbH), a dual cone mixer equipped with double helical mixer blades (Design Integrated Technologies), a batch melt mixer (Brabender W50EH), and a twin-screw extruder (Werner & Pfleiderer ZSK25). Typically, the carefully dried prepolymer powder was charged into the preheated reactor. When the prepolymer was completely molten, the chain extender was added, proportional to the concentration of end-groups. The course of the reactions was followed by means of torque-vs.-time curves and by taking samples.

Elastomers for rubber-modification studies were polymerized as follows. Poly(ester-urethanes) based on poly(L-lactic acid-co-ε-caprolactone) prepolymers were synthesized in a two-step process described above. L-lactide/ε-caprolactone copolymers were synthesized by ring-opening polymerization from L-lactide and ε-caprolactone monomers. The copolymerization was carried out in bulk at 140°C for 28 h with $Sn(Oct)_2$ as initiator and glycerol as co-initiator. The composition of elastomers is expressed as mol% monomer in the feed, and thus, P(L-LA40/CL60), P(L-LA60/CL40), P(L-LA80/CL20), and P(LA40/CL60)U, expressed as wt.% in publication III, are changed to P(L-LA35/CL65), P(L-LA54/CL46), P(L-LA76/CL24), and P(LA46/CL54)U.

2.3 Blending and processing

Poly(ester-urethane) blends with rubbers and fillers were prepared with a batch mixer (Haake Rheomix 600 or Brabender W50EH) or with a co-rotating twin-screw midiextruder (DSM, Netherlands; screw length 150 mm) equipped with a back-flow channel that allows it to be operated in batch wise.

Test specimens for dynamic mechanical thermal analysis and impact and tensile testing were prepared by compression molding (Fontijne or Darragon) or by injection molding with a mini-injection molding machine (DSM).

2.4 Characterization

Molecular weights and molecular weight distributions were determined by room temperature size exclusion chromatography, SEC (Waters System Interface module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 700 Satellite Wisp, and four PL gel columns: 10^4 Å, 10^5 Å, 10^3 Å, and 100 Å connected in series). Chloroform was used as solvent and eluent. The injected volume was 200 µl and the flow rate 1 ml/min. Monodisperse polystyrene standards were used for calibration. Acid values (AV), defined as the weight in milligrams of potassium hydroxide required to neutralize 1 g of the polymer, were determined by titrimetric methods. The samples

were dissolved in chloroform and titrated against 0.01 M KOH in ethyl alcohol solution in the presence of α-naphtholphthalein indicator.

The thermal properties were determined using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The DSC measurements (Polymer Laboratories or Mettler Toledo Star^e DSC821) were carried out over a temperature range of -80 to 180 °C and a heating and cooling rate of 10 °C/min. Glass transition temperatures were recorded during the second heating scan to ensure identical thermal histories. The DMTA measurements were carried out using the three-point bending method (Perkin Elmer 7 Series) or dual cantilever geometry (RSA, Rheometrics).

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-FTIR 750 spectrometer, using compression molded film samples or film samples cast on a potassium bromide plate from chloroform solutions. Proton decoupled ^{13}C NMR spectra with NOE and ^{1}H NMR spectra were obtained at room temperature with a Varian Gemini 2000 300 MHz spectrometer working at 75.452 MHz for carbons and at 300.032 MHz for protons or with Varian Unity 400 spectrometer working at 100.557 MHz for carbons (I, II). The sample concentrations were 10 wt.% in 10-mm tubes for ^{13}C NMR and 1 wt.% in 5-mm tubes for ^{1}H NMR in $CDCl_3$ (deuteration degree not less than 99.8%).

The morphology of a cross-section of the cryogenically fractured samples was examined by scanning electron microscopy, SEM (Zeiss Digital Scanning Microscope 962 or Cambridge Instruments, Stereoscan 120). SEM micrographs were taken after coating the surfaces with a thin layer of platinum or gold.

The tensile and impact properties of the polymers were measured for parallel air-conditioned specimens that had been left for 72 hours at 23°C and 50% relative humidity. Tensile properties were evaluated with an Instron 4204 or an Instron 8031 tensile testing machine. The tensile tests of the non-standard compression molded and sawn samples were characterized according to the ISO/R 527-1966(E) standard or according to standard ISO/R 527-1993(E) for injection molded samples. Charpy impact tests of unnotched specimens were performed on Zwick pendulum-type testing machine. Injection molded or compression molded samples with dimensions of $4\times6\times50$ mm^3 were measured according to ISO 179/2D f or ISO 179-1982(E) standards, respectively.

The dynamic rheological measurements were carried out on a Rheometric Scientific stress-controlled dynamic rheometer SR-500. The unstabilized specimens, prepared with the mini-injection molding machine, were dried in vacuum for 24 hours before rheological characterization. All measurements were made in the linear viscoelasticity region, which was ensured through a stress sweep. Rheological characterization was performed under nitrogen using 25-mm cone-plate geometry with a sample gap of 0.045 mm. In frequency sweeps, the angular frequency range was from 0.02 to 100 rad/s and a stress equivalent to 2% strain was used.

3 RESULTS AND DISCUSSION

3.1 Modification by copolymerization

Modification of lactic acid based poly(ester-urethane) by copolymerization is discussed in publications I and II. The unmodified poly(ester-urethane) loses its mechanical properties at about 50°C, and thus particular attention was focused on improving the heat resistance of the polymer. In publication I, the copolymers of L-lactic acid (LLA) with DL-mandelic acid (DLMA), 4-hydroxybenzoic acid (HBA), 4-acetoxybenzoic acid, DL-malic acid (MLA), or anhydrous citric acid (CAA) were synthesized via direct copolycondensation to produce prepolymers for the urethane synthesis with increased chain stiffness.

Another approach was, with a new flexible material in mind, to introduce elastomeric properties to lactic acid polymers by preparing copolyesters from lactic acid and ε-caprolactone (publication II). Poly(L-lactic acid-co-ε-caprolactone-urethanes) would possess variable properties, from hard plastics to flexible materials, and thus be valuable biodegradable materials.

3.1.1 Introduction of stiff groups into the PEU chain

L-lactic acid was condensation polymerized with various comonomers in the presence of 3 mol% 1,4-butanediol and $Sn(Oct)_2$ as a catalyst. All copolymers were hard and brittle oligomers, and completely amorphous, which is typical for polycondensed lactic acid oligomers. Racemization is caused by the catalyst used, high polymerization temperature, and long reaction times.

The copolymerizations of L-lactic acid and another hydroxy acid, DL-mandelic acid, were investigated over a composition ranging from 5 to 45 mol% of DLMA (Figure 3). The glass transition temperature increased with an increase in mandelic acid composition in the copolymer, as shown in Figure 4. Large and bulky side groups restrict rotation of the polymer chain and cause an increase in T_g from 33 to 56°C. Phenyl groups also cause steric hindrance, depressing the rate of copolymerization. Copolymers of LLA and p-hydroxybentzoic acid had even lower molecular weights than LLA/DLMA copolymers. The number average molecular weight dropped from 4400 to 1200 g/mol when the amount of HBA was increased from 0 to 20 mol%. Due to the low molecular weights, the glass transition temperatures of LLA/HBA copolymers did not increase as expected; T_g was practically constant around 33 - 35°C.

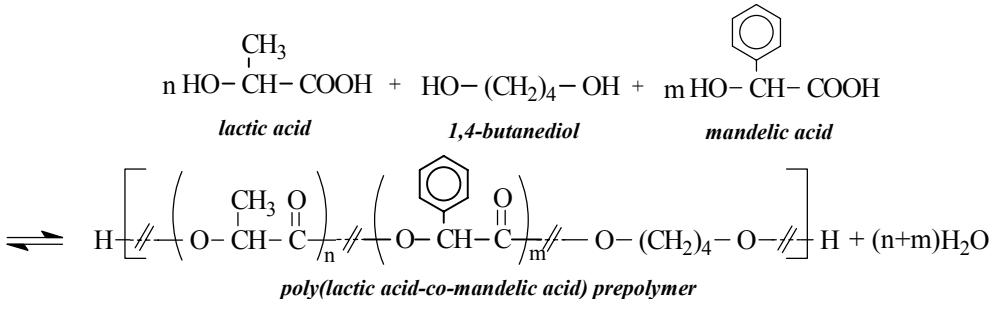

Figure 3. Copolymerization of lactic acid and mandelic acid. (I)

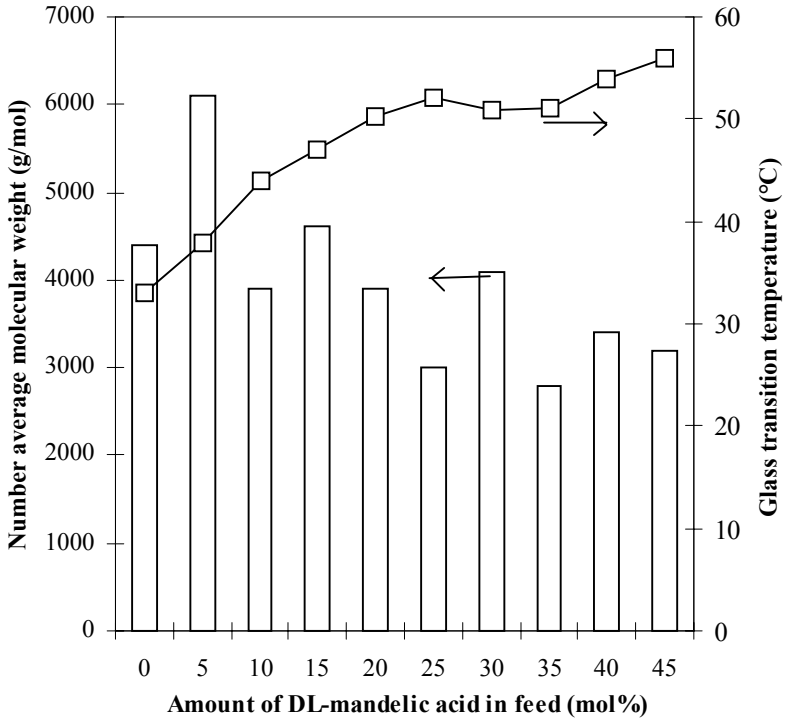

Figure 4. The effect of mandelic acid on T_g and $\overline{M}_n$ of poly(L-lactic acid-co-DL-mandelic acid) oligomer in test tube polymerizations.(data from publication I)

The copolyesters from LLA and trifunctional DL-malic acid, and from LLA and four-functional anhydrous citric acid were bright and especially hard. Even a small quantity (< 5 mol%) of MLA or CAA increases the glass transition temperature by 9 - 11EC. A high density of branching, or long-chain branching will have the same effect as side groups in restricting chain mobility, hence raising T_g. The drop in T_g values in LLA/MLA and LLA/CAA copolyesters with higher MLA and CAA concentrations was probably due to the decrease in molecular weight, formation of low-molecular weight cyclic structures, and self-condensation reactions of multifunctional comonomers.

Poly(L-lactic acid-co-DL-mandelic acid-urethanes) were synthesized by linking LLA/DLMA prepolymers with aliphatic 1,6-hexamethylene diisocyanate (HMDI) or cycloaliphatic isophorone diisocyanate. The steric hindrance of the bulky phenyl group of mandelic acid, residual small molecular weight compounds and, as discovered in later studies, high residual acid content of prepolymers despite the use of BD (2 mol%), adversely affects the reaction between polyester prepolymers and isocyanates. These factors increase the consumption of HMDI and favor the side reactions. Thus, the molecular weights of the copolymers were lower than those of PEU's based on poly(L-lactic acid) prepolymer. Molecular weight distributions were very wide and some samples were partially insoluble, suggesting the formation of branches and crosslinks. The reaction between -OH and -NCO groups was even more restricted when isophorone diisocyanate was used; consequently the molecular weights were low, molecular weight distributions were narrow, and the

materials were very brittle. The properties of poly(ester-urethanes) linked with HMDI are presented in Table 1.

Table 1. Prepolymer compositions, molecular weights, glass transition temperatures, and tensile properties of poly(L-lactic acid-co-DL-mandelic acid-urethanes).(I)

Prepolymer composition in feed (mol%)			*SEC*			*DSC*	*Tensile properties*		
			M_n	M_w	*MWD*	T_g	*Tensile modulus*	*Tensile strength*	*Maximum strain*
LLA	*DLMA*	*1,4-BD*	*(g/mol)*	*(g/mol)*		*(°C)*	*(MPa)*	*(MPa)*	*(%)*
98	-	2	41 000	187 000	4.6	53	1930 ± 60	47 ± 2	3.7 ± 0.3
89.1	8.9	2	16 000	116 000	8.0[a)]	58	2010 ± 60	34 ± 8	1.8 ± 0.4
78.9	19.1	2	23 000	120 000	6.7[a)]	60	2010 ± 20	49 ± 1	3.1 ± 0.1

a) End product partially insoluble in chloroform

The introduction of DLMA comonomer, which impedes rotation and stiffens the chain clearly causes a large increase in the glass transition temperature of PEU. Using 10 and 20 mol% of DL-mandelic acid in copolyester, the T_g of poly(ester-urethane) increased from the initial value of 53°C to 58 and 60°C, respectively. The highest T_g of 63°C measured by DSC was achieved with isophorone diisocyanate and 10 mol% DLMA. DMTA analysis established the marked improvements in the heat resistance measured from the peak value of tan δ (T_g) and the onset of storage modulus, as seen in Figure 5. Although the molecular weights were lower, the values of storage modulus and mechanical properties of poly(L-lactic acid-co-DL-mandelic acid-urethanes) shown in Table 1 were comparable with PEU based on lactic acid.

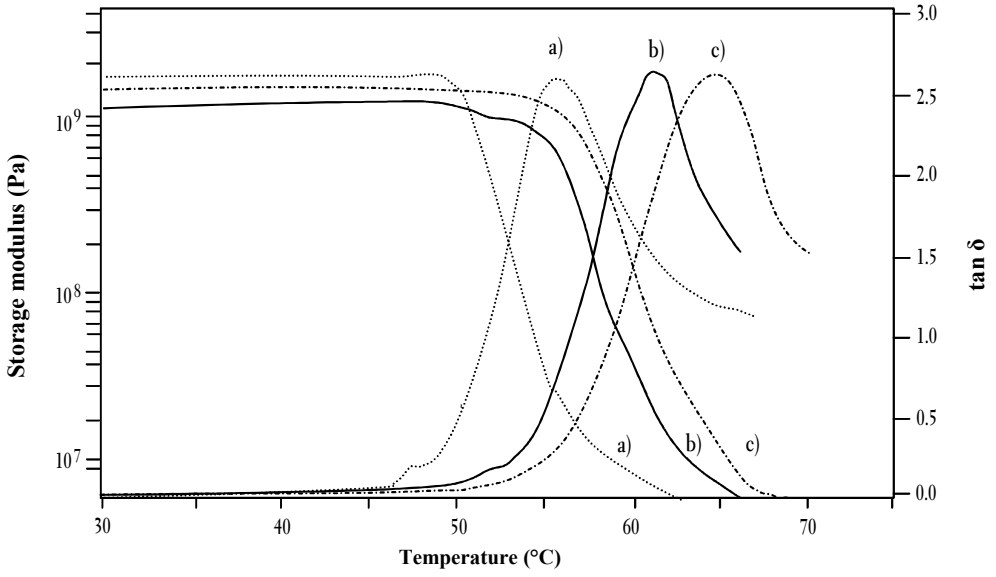

Figure 5. DMTA storage modulus and tan δ curves of poly(L-lactic acid-co-DL-mandelic acid-urethanes) LLA/DLMA compositions of a) 100/0, b) 90/10, and c) 80/20 (mol% in feed).(I)

3.1.2 Imparting elastomeric properties to poly(ester-urethane)

The copolymerization of L-lactic acid and ε-caprolactone (CL) prepolymer was investigated over a wide range of composition (II). The LA/CL copolymers were low molecular weight hydroxyl terminated oligomers, with a physical appearance that varied widely with monomer composition from solid to waxy. The structure of the copolymers was determined by ^{13}C NMR analysis. The results showed the copolymer composition to be in satisfactory agreement with the comonomer feed ratio: copolymer compositions were within 0.4 - 8.8% of the initial feed ratios (Table 2). The sequence analysis results showed that the copolymers had short average block lengths, which means that they are statistical. Indeed, at a LA/CL monomer composition of 50/50 mol% the average block lengths were more or less equal (2.0 vs. 2.1).

Like homopolymerization, the optical activity of lactic acid units changes during the condensation copolymerization, which leads to an amorphous copolymer, even with high LA content. The amounts of different configurational structures, i.e. D-lactic acid structures in the polymer chains, were fairly large in LA-rich copolymers (about 20 mol%), but still typical of values found in the polycondensation of L-lactic acid. When the content of CL in the copolymer was increased above 30 mol%, the amount of different optical isomers was less than 10 mol%. Only the CL-rich oligomer (LA25/CL75) exhibited slight crystallization, but it still produced amorphous poly(ester-urethane).

The five methylene groups in ε-caprolactone units build flexibility into the polymer chain and lower the glass transition temperature. As seen in Figure 6, T_g decreases with an increase in CL content in the copolymer. The experimental values are a little lower, but still in a very good agreement with the Fox equation[135], which is frequently used to predict T_g of random copolymers.

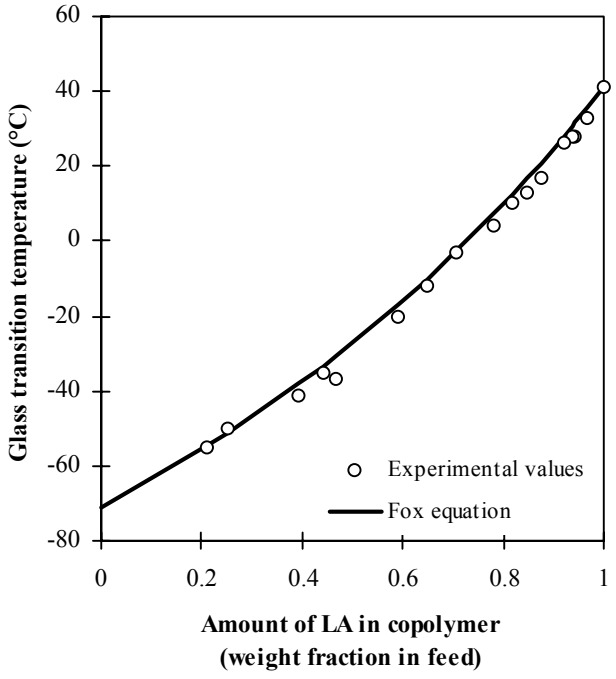

Figure 6. Glass transition temperature of (L-lactic acid-co-ε-caprolactone) oligomers and Fox equation plotted against the amount of L-lactic acid.(II)

High molecular weight thermoplastic poly(L-lactic acid-co-ε-caprolactone-urethanes), P(LA/CL)U, were synthesized by reacting hydroxyl-terminated (LA/CL) prepolymers and HMDI. The properties of amorphous P(LA/CL)U are summarized in Table 2. The thermal properties of these polymers correlate with the properties of the prepolymer: increase in molecular weight and the formation of hydrogen bonds increases T_g of the poly(ester-urethane) by about 9-12°C compared with the parent polyester prepolymer. The physical appearance of thermoplastic poly(ester-urethane) depends on the monomer composition in the prepolymer. Polymers with high lactic acid content were rigid plastics, while CL-rich polymers were elastomeric due to the flexible nature of the caprolactone repeating unit.

The tensile properties of the PEUs were dependent on the glass transition temperature. As long as the temperature is below the T_g of the polymer, polymer chains will be fairly immobile and able to contribute to the strength of the material. Poly(ester-urethane) containing only lactic acid is hard and brittle, having a high tensile modulus of about 2 GPa, a tensile strength of 47 MPa, and a maximum strain of 3.5%. Small amounts of ε-caprolactone increased the maximum strain, whereas tensile modulus and maximum stress decreased in proportion to the CL content. All polymers with less than 10 mol% CL in the prepolymer exhibited plastic properties, whereas other polymers exhibited typical rubber properties and managed to recover completely from more than 1000% extension.

To investigate the effect of configurational structure, prepolymers were also prepared from DL-lactic acid (DLLA) in the same way and with the same CL content as (LA70/CL30). Neither the polymerization of the prepolymers nor the polyurethane synthesis was configuration dependent: molecular weights, as well as thermal and mechanical properties were comparable.

Table 2. Properties of poly(ester-urethane) elastomers.(II)

Urethane (mol/mol)	*^{13}C NMR composition in copolymer (mol LA/mol CL)*	*T_g (DSC) (EC)*	*Tensile modulus (MPa)*	*Maximum stress (MPa)*	*Maximum strain (%)*
PEU	100 / 0	53	1900 ± 60	47 ± 2	3.7 ± 0.3
P(LA97/CL03)U	97.1 / 2.9	45	2100 ± 50	43 ± 1	4.7 ± 1.7
P(LA96/CL04)U	94.7 / 5.3	40	1700 ± 130	36 ± 1	6.9 ± 4.6
P(LA94/CL06)U	93.0 / 7.0	35	1300 ± 130	23 ± 3	420 ± 20
P(LA88/CL12)U	86.8 / 13.2	28	80 ± 20	8.6 ± 0.4	440 ± 40
P(LA76/CL24)U	74.3 / 25.7	9	1.7 ± 0.6	0.4 ± 0.1	> 1000
P(LA70/CL30)U	68.5 / 31.5	-3	1.4 ± 0.1	1.5 ± 0.2	> 1000
P(LA65/CL35)U	63.7 / 36.3	-5	1.5 ± 0.2	1.6 ± 0.1	900 ± 50
P(LA53/CL47)U	45.7 / 54.3	-24	1.6 ± 0.3	0.2 ± 0.1	730 ± 70
P(LA50/CL50)U	47.9 / 52.1	-26	1.5 ± 0.3	1.6 ± 0.3	> 1000
P(LA30/CL70)U	27.0 / 73.0	-45	1.7 ± 0.1	1.8 ± 0.1	590 ± 50
P(LA25/CL75)U	20.9 / 79.1	nd.	5.3 ± 1.4	0.09 ± 0.01	> 1000
P(LA35DLLA35/CL30)U	69.1 / 30.9	-3	1.1 ± 0.1	1.3 ± 0.3	>1000
P(DLLA70/CL30)U	69.4 / 30.6	-4	1.4 ± 0.3	1.5 ± 0.3	940 ± 170

nd. not detected

3.2 Effect of chain linking on the properties of PEU

The chain linking of lactic acid oligomers is not only an economically feasible technology for producing high molecular weight polyesters but it also offers great possibilities for structure modifications. Improved mechanical properties and flexibility in manufacturing polymers and copolymers with different functional groups are associated with the use of chain extending agents. In this section, the modification of the properties of PEU by changing the amount of chain extending agent (publication VI and VII) and by introducing an other type of chain extender and a new chain linking technique (publication VII) are discussed.

The very high reactivity of the isocyanates has encouraged their use for coupling or chain extension of oligomers. In the polymerization of lactic acid based poly(ester-urethane), the chain extending reactions of diisocyanate take place by addition across the C=N double bond with an equimolar amount of -OH groups in the hydroxyl-terminated prepolymer. In the studied system, diisocyanates are able to react with carboxylic acid groups or with moisture, as well as with formed urethane bonds to form allophanates or with each other in isocyanate homopolymerization. Thus, the chain extending reaction must compete with other reactions, even though these side reactions are significantly slower. The last two reactions, when an excess of diisocyanate is used, lead to branching in the polymer, which greatly affects the flow properties of the polymer melt. Through the modification of rheological properties, improvements in the performance of polymers in particular applications, such as extrusion coating of paper, can be achieved.

To avoid the problem of different kinetic reaction rates of chain linking, PLA oligomers are usually modified to the hydroxyl or carboxyl terminated form with the use of small amounts of difunctional compounds. Typically, 1,4-butanediol or adipic acid have been used.[136] Even small quantities of these compounds have an effect on the properties, such as the glass transition temperature of the obtained polymers. However, the use of two chain extenders having different functional groups has certain advantages. The molecular weight is increased by the coupling of two macromolecules and the content of both terminal groups can be decreased, which leads to improved thermal stability. In addition, new groups are introduced to the reaction system and subsequently onto the polymer chain.

3.2.1 Modification of rheological properties within HMDI linking

Varying the OH/NCO ratio, i.e., increasing the amount of chain extender in polymerization, had several effects on the polymerization and the structure of the chain, and subsequently on the properties of the resulting poly(ester-urethanes). With hydroxyl-terminated prepolymer at equimolar amount of diisocyanate relative to -OH groups, the weight average molecular weight (M_w) increased rapidly within the first few minutes, as seen in Figure 7. An increase in the amount of chain extender prolonged the polymerization time in such a way that maximum torque and molecular weights were achieved at 80 and 100 min for OH/NCO ratios of 1:1.1 and 1:1.2, respectively. In addition, the M_w curves gradually became flatter at the beginning of the reaction.

According to ^{13}C NMR, hydroxyl groups in the prepolymer are consumed at the start of the polymerization and the excess of diisocyanate is assumed to produce NCO-terminated polymers, which retain the reactivity of the isocyanate. Further increase in the molecular weight is prevented by the lack of -OH groups. Isocyanate groups can further react with -OH or -COOH groups formed by the thermal degradation of the poly(lactic acid) chain. However, the observed gradual increase in M_w during the reaction and faster increase at a certain point of the polymerization is caused by the reactions of NCO-terminated polymers with urethane bonds, producing allophanates, and so branching and crosslinking. Concurrent with the fast increases in M_w, the number average molecular weight remains essentially unchanged for the whole period of time. This is observed as an instant broadening of the molecular weight distribution from 2 to 4.5 (Figure 7, bold lines). However, samples were thermoplastic and soluble in chloroform, and gel fractions were not observed. With a further increase in the amount of chain extender the gelation became dominant.

After reaching the maximum, a decrease in weight average molecular weight occurred, especially in the samples with OH/NCO ratios of 1:1.1 and 1:1.2. This is due to lack of reactive groups and degradation of the thermally unstable ester bond on the lactic acid chains. Poly(lactic acids) are typically highly sensitive to thermal degradation during polymerization and processing.

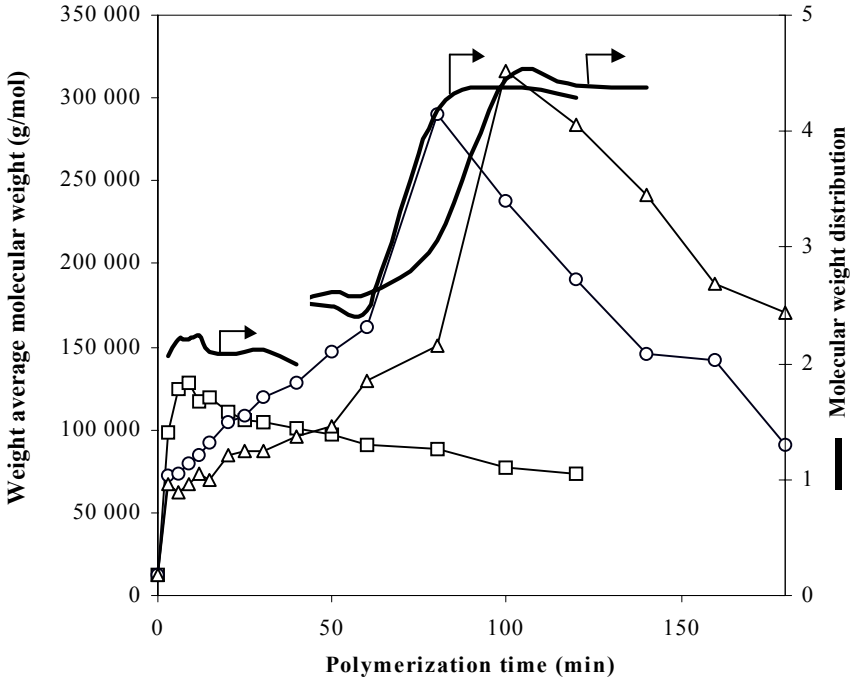

Figure 7. Development of the weight average molecular weight and molecular weight distribution (bold line) for prepolymer E2% with OH/NCO ratios of 1:1.0 (~), 1:1.1 (¯), and 1:1.2 (ª). (VII)

Hydroxyl-termination is essential for the polymerization to reach high molecular weights. Among the required qualities of prepolymers for the polyurethane synthesis, acid value is of particular importance, since it is a measure of the residual amount of carboxyl end-groups. The reaction between an isocyanate group and a carboxyl group leads to the formation of an amide linkage, but the reaction is much slower. Moreover, the residual acid content of the polyester negatively affects the polyurethane reaction and decreases the stability of the poly(ester-urethane). Thus, a higher level of acid groups appears to slow the linking reaction and the chain extender is consumed in excess of the theoretical values, which are based on hydroxyl group determination.

Molecular weight, molecular weight distribution, and long-chain branching are the primary factors affecting the viscoelasticity of the polymer, and all of these can be studied through rheological measurements. High viscosity at low shear rates, and elasticity, are desired properties for polymers in extrusion coating, whereas low viscosity is advantageous for overall processing. All three requirements can be met through strong shear thinning, and normally they are achieved by producing long-chain branching or broadening the MWD.

Dynamic frequency sweeps were used to determine differences in the structures of the polymers. The properties of the studied PEU samples, whose chain structure modification was made by varying the amount of chain extender from 1:1.1 to 1:1.3 (OH/NCO ratio; publication VI), are shown in Table 3.

Table 3. Properties of poly(ester-urethane) samples used in dynamic rheometer measurements.(VI)

Polymer	*OH/NCO*	M_n *(g/mol)*	M_w *(g/mol)*	*MWD*
P12-110	1:1.1	45 000	104 000	2.3
P12-120	1:1.2	47 000	135 000	2.9
P12-130	1:1.3	57 000	179 000	3.2

Clear differences were evident in the rheological properties of PEU samples, as can be seen in Figure 8. Complex viscosities were higher for samples with higher weight average molecular weights. These samples already showed shear thinning at low frequencies, which is, as mentioned, typical for polymers whose molecular weight distribution is broad or polymers having long-chain branching. The storage and loss modulus were also higher for samples with broader MWD. An increase in the storage modulus indicated improved elasticity. An increase in MWD from about 2.3 to 2.9 had a noticeable effect on the viscoelastic properties of the samples. However, a change from 2.9 to 3.2 increased the complex viscosity and storage modulus of the samples considerably more.

Rheological properties are most affected by the longest polymer chains and branching, which has to be taken into consideration when studying the influence of MWD on viscoelasticity. Unfortunately, long-chain branching and broad MWD have similar effects on the viscoelastic properties, and thus long-chain branching as an explanation of the behavior of the sample P12-130 cannot be independently verified by rheological measurements. However, side reactions during the

polymerization lead to branching in the polymer when an excess amount of chain extender is used. Some peaks in the ^{13}C NMR spectra, which are not characteristic for linear poly(ester-urethane), can be found for samples with a high excess of isocyanate. These peaks are at 31.1 and 42.9 ppm, close to peaks due to the CH_2 groups of hexamethylene diisocyanate in linear PEU, and at 155.4 ppm, close to the peak of the urethane bond. Because the peak of free isocyanate at 122.0 ppm appeared only in the spectra where the amount of chain extender led to crosslinking, new peaks can be attributed to the above-mentioned side reactions of NCO-terminated polymers. Increased branching leads to crosslinking of the polymer, i.e. at first the polymer is branched, and finally, with a high excess of chain extender, the polymer chains are crosslinked. This can be proved by gel contents determined by extraction, in the decreased solubility of the polymers in general, and in their rheological properties.

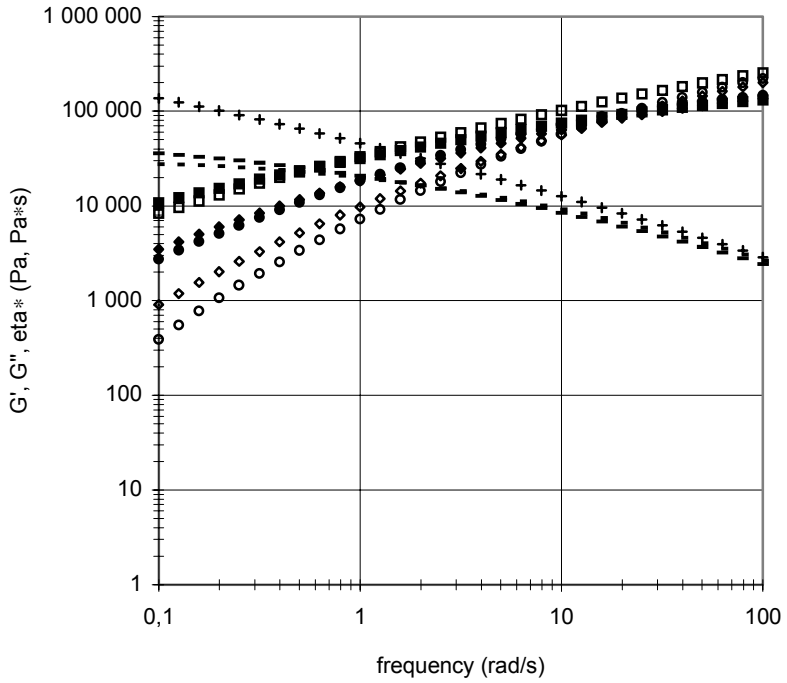

Figure 8. Storage (G') and loss (G") moduli and complex viscosity (eta*) for PEU samples, measured at 120°C with a dynamic rheometer (strain 2%): P12-110 (G' ¯, G" C, eta* -), P12-120 (G' ¡, G" , , eta* –), and P12-130 (G' ~, G" , eta* +).(VI)

3.2.2 The use of two chain extending agents

In study VII, novel L-lactic acid polymers were synthesized with the use of highly effective hydroxyl reactive 1,6-hexamethylene diisocyanate, and carboxyl reactive 2,2'-bis(2-oxazoline) (BOX) chain extenders. The purpose of adding BOX is for it to react with carboxyl end-groups of the lactic acid oligomer and thus lower the acid value. At the same time, difunctional BOX couples two oligomers to the hydroxyl-terminated prepolymer, which can be further chain extended with

diisocyanate. This make it possible to prepare hydroxyl-terminated prepolymer for urethane synthesis without the use of diol compound. This, in turn, by the amount used defines the number of polymer chains, and thus the maximum molecular weight of prepolymer that can be obtained: the more BD is used, the lower the molecular weight. Therefore, the addition of a highly reactive coupling agent during the final steps of melt polycondensation of polyester allows the production of higher molecular weight prepolymers, with lower acid values. Since effective diisocyanate linking reactions require low acid values, which are reached with very long condensation times at high temperature and low pressure, the main technology advantages of this kind of technique on the polymerization of prepolymers are the shorter condensation time and lower temperature required. With lactic acid polymers, in particular, the shorter polymerization time and lower temperature will reduce thermal degradation and lactide formation.

The effect of the amount of 2,2'-bis(2-oxazoline) on the acid value of prepolymer E0% (initial lactic acid oligomer having a hydroxyl group at one end of the polymer chain and a carboxyl group at the other) is seen in Figure 9a. In 30 min reaction time, an equimolar amount of BOX end-groups (OX) to the carboxyl groups decreased the acid value from 11 to 5, whereas without BOX the acid value of the prepolymer increased slightly, owing to thermal degradation. When the ratio of COOH/OX was changed from 1:1 to 1:2, the acid value decreased faster and fell to a considerably lower level. Since the molecular weight increases in proportion to the BOX content (Figure 9b), obtaining prepolymer with doubled molecular weight at a large excess of 2,2'-bis(2-oxazoline) confirms the greater effectiveness of BOX coupling compared with the blocking reaction, i.e. reaction where only one of the two rings have reacted.

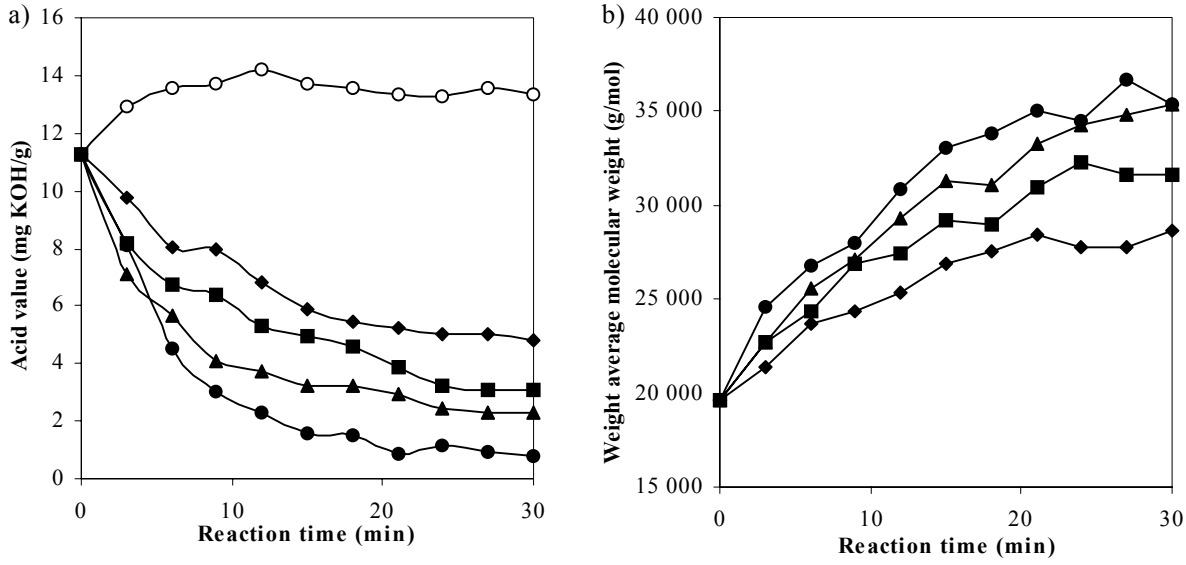

Figure 9. Effect of COOH/OX ratio on a) acid value and b) weight average molecular weight of prepolymer E0%: plain polymer without BOX (¯), COOH/OX ratio of 1:1.0 (,), 1:1.1 ( ), 1:1.4 (•), and 1:2.0 (⁻).(VII)

In the combination chain linking polymerizations, BOX was allowed to react for a defined time before HMDI was fed to the reaction system. Both chain coupling agents were found to react selectively with end-groups, forming oxamide and urethane groups, as characterized by FTIR and ^{1}H NMR spectroscopy. In addition, it was deduced from the measurements that the 2-oxazoline group did not react with an isocyanate group.

Figure 10 shows the development of the weight average molecular weight during the polymerization for E0% with OH/NCO ratios of 1:1.0, 1:1.1, and 1:1.2. The BOX ratio of 1:2 with 20 min reaction time decreased the acid value from 11.3 to as low as 1.5. The molecular weight increased rapidly after diisocyanate addition and M_w reached the high level of 200 000 g/mol. The development of the molecular weight was also dependent on the amount of HMDI, similar to that for the hydroxyl-terminated prepolymer in Figure 7. The clear difference was that the rapid leap in weight average molecular weight seen earlier, especially as broadening of the molecular weight distribution, was absent in these BOX-HMDI combination chain linking polymerizations.

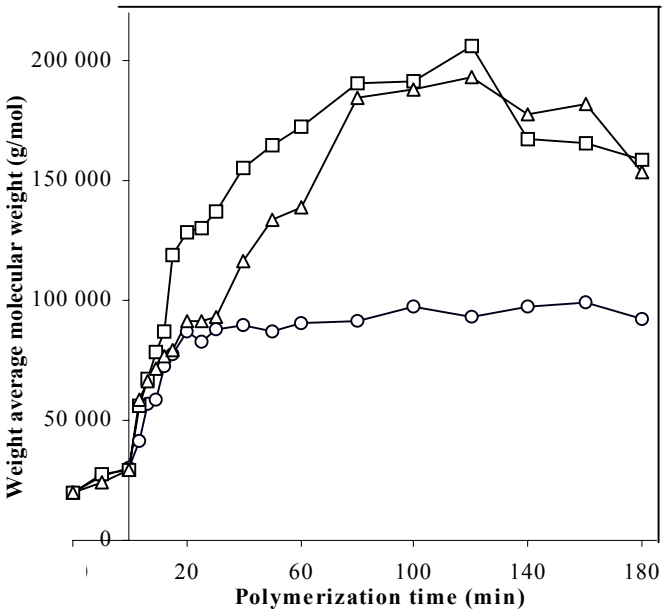

Figure 10. Molecular weight development versus polymerization time for oligomer E0% chain linked with 2,2'-bis(2-oxazoline) (COOH/OX ratio 1:2) and with different amounts of hexamethylene diisocyanate: OH/NCO ratios of 1:1.0 (¯), 1:1.1 (~), and 1:1.2 (Î).(VII)

The result of the HMDI chain extending is modest if the amount of BOX is not high enough, or the reaction time of BOX is not long enough to reduce the number of acid end-groups before HMDI addition. With the ratio of COOH/OX 1:1.1, provided that the reaction time was adequate, the obtained molecular weights were more or less equal (170 000 - 190 000 g/mol), although the acid values were still fairly high (5-7). However, the increase in the reaction rate at the beginning of the polymerization is more dramatic in the case of lower acid value.

The important observation in these BOX-HMDI combination polymerizations was that an excess amount of BOX caused a significant improvement in the thermal stability of the resulting polymers. By reacting with new carboxyl groups, which are formed by the thermal degradation of poly(lactic acid) chains, oxazoline end-groups prevent the observed drop in molecular weight after reaching the maximum. However, it was interesting that the molecular weights stayed at the highest level for as long as 40 min. This is important from the practical point of view, eg. further processing.

The introduction of oxamide groups into the polymer structure increased the chain stiffness, which was detected in mechanical properties and as an increment in the glass transition temperature. Differences between representative samples of the synthesized polymers were compared: prepolymer E0% chain linked with BOX (COOH/OX ratio of 1:2) and with HMDI (OH/NCO ratio of 1:1.1) (designated hereafter as P0%), and hydroxyl terminated prepolymer chain linked with HMDI (OH/NCO ratio of 1:1.1) (designated as P2%). Compositions, molecular weights and mechanical properties of samples P0% and P2% are presented in Table 4. Thus, there are two main factors differentiating the structures of P0% and P2%. The introduction of stiffer BOX units to replace half of the HMDI units stiffens the polymer chains of P0% compared to P2%. Also, 2 mol% of 1,4-butanediol increases the chain flexibility and mobility even more in P2%. A slight difference in tensile modulus and strength was detected due to the difference in polymer structure. Similarly, the chain flexibility caused a marked difference in strain between the two polymers.

Table 4. Mechanical properties of lactic acid polymers.(VII)

Sample	*BD (mol%)*	*COOH/ OX ratio*	*OH/ NCO ratio*	*M_n (g/mol)*	*M_w (g/mol)*	*MWD*	*Tensile modulus (MPa)*	*Tensile strength (MPa)*	*Strain at break (%)*
P2%	2	-	1:1.1	63 000	188 000	3.0	1640 ± 30	55 ± 4	11 ± 2
P0%	0	1:2	1:1.1	53 000	162 000	3.0	1750 ± 20	57 ± 3	6 ± 3

The storage modulus was also considerably higher for P0%. This is seen in Figure 11, where storage modulus (E'), loss modulus (E''), and tan δ as a function of temperature obtained from dynamic mechanical thermal analysis are plotted. The values of the E'' and tan δ peak temperatures are higher for P0%. The loss modulus values were 52°C and 55°C for P2% and P0%, respectively. These values of glass transition temperature are closely related to the polymer structure. 1,4-butanediol and a larger amount of HMDI units with six flexible aliphatic methylene groups increase the chain flexibility and mobility, and cause a decrease in the T_g. The effect of BD was already detected in the prepolymers.

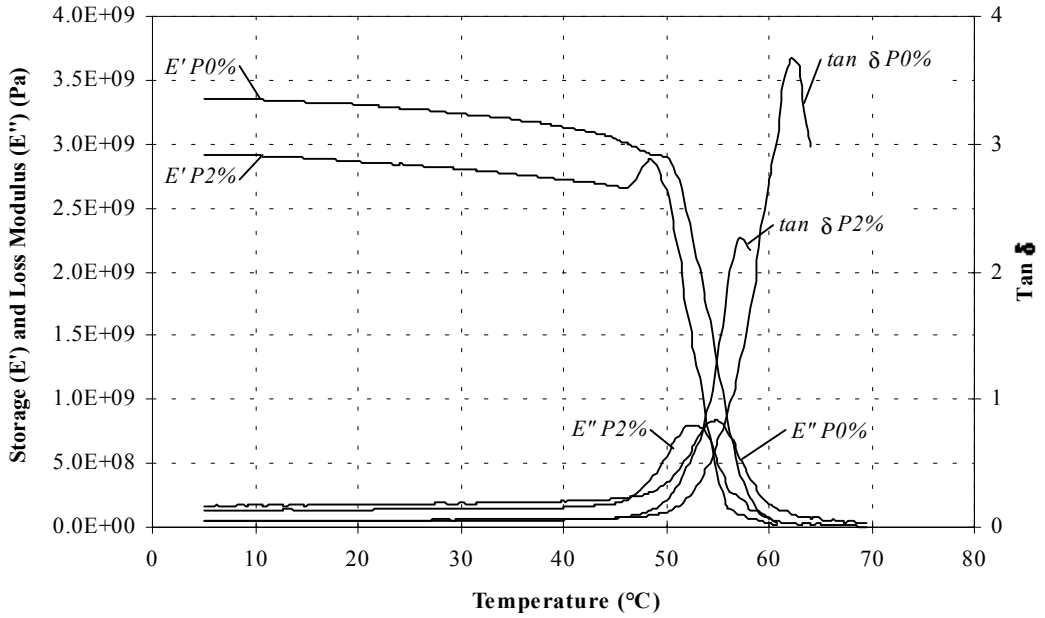

Figure 11. DMTA plot of polymers P2% and P0%.(VII)

3.3 Blending of poly(ester-urethane)

3.3.1 Impact modification of poly(ester-urethane)

The rubber modification of poly(ester-urethane) was studied in publications III and IV to overcome its inherent brittleness. PEU was melt-blended with 5-30 wt.% of two different biodegradable elastomers. Elastic copolymers of L-lactide and ε-caprolactone, P(L-LA/CL), were synthesized by ring-opening polymerization, whereas poly(L-lactic acid-co-ε-caprolactone-urethane), P(LA/CL)U, elastomers were prepared by direct polycondensation of L-lactic acid and ε-caprolactone followed by diisocyanate linking, as described earlier and in publication II. In both these elastomers, the composition of comonomers was varied. Contrary to publication III, the numbers in parenthesis below describe the monomer composition in the feed in mol%, except in section 3.1.1.1, where compositions are expressed as wt.% in the feed to achieve an appropriate comparison. As a matrix polymer, two types of poly(ester-urethane) were used, linear and branched as described in Chapter 3.2.1.

3.3.1.1 Type of rubber

Copoly(L-lactide/ε-caprolactone) and poly(L-lactic acid-co-ε-caprolactone-urethane) have a very similar chemical structure. The main difference in the structure units is the urethane bonds of P(LA/CL)U, which on the other hand brings it closer to the structure of the poly(ester-urethane) matrix. All blends of linear PEU and different amounts of P(L-LA40/CL60) or P(LA40/CL60)U

(wt.%/wt.%) elastomers revealed a two-phase morphology, exhibiting two separate glass transitions corresponding to the T_gs of the rubber and the matrix, as seen from DMTA measurements in Figure 12a and 12b. In PEU/P(L-LA40/CL60) blends, the T_g of the matrix phase remains unchanged, apart from a slight broadening of the peak. In contrast, the T_g of the PEU phase in PEU/P(LA40/CL60)U blends was shifted gradually with increasing rubber content towards the T_g of the rubber phase, indicating some miscibility and interactions between the phases. SEM micrographs (Figure 12c and 12d) revealed a two-phase morphology with rubbery copolymer particles. The P(LA/CL)U particles were not as round as the P(L-LA/CL) particles, and the average particle size was also slightly smaller.

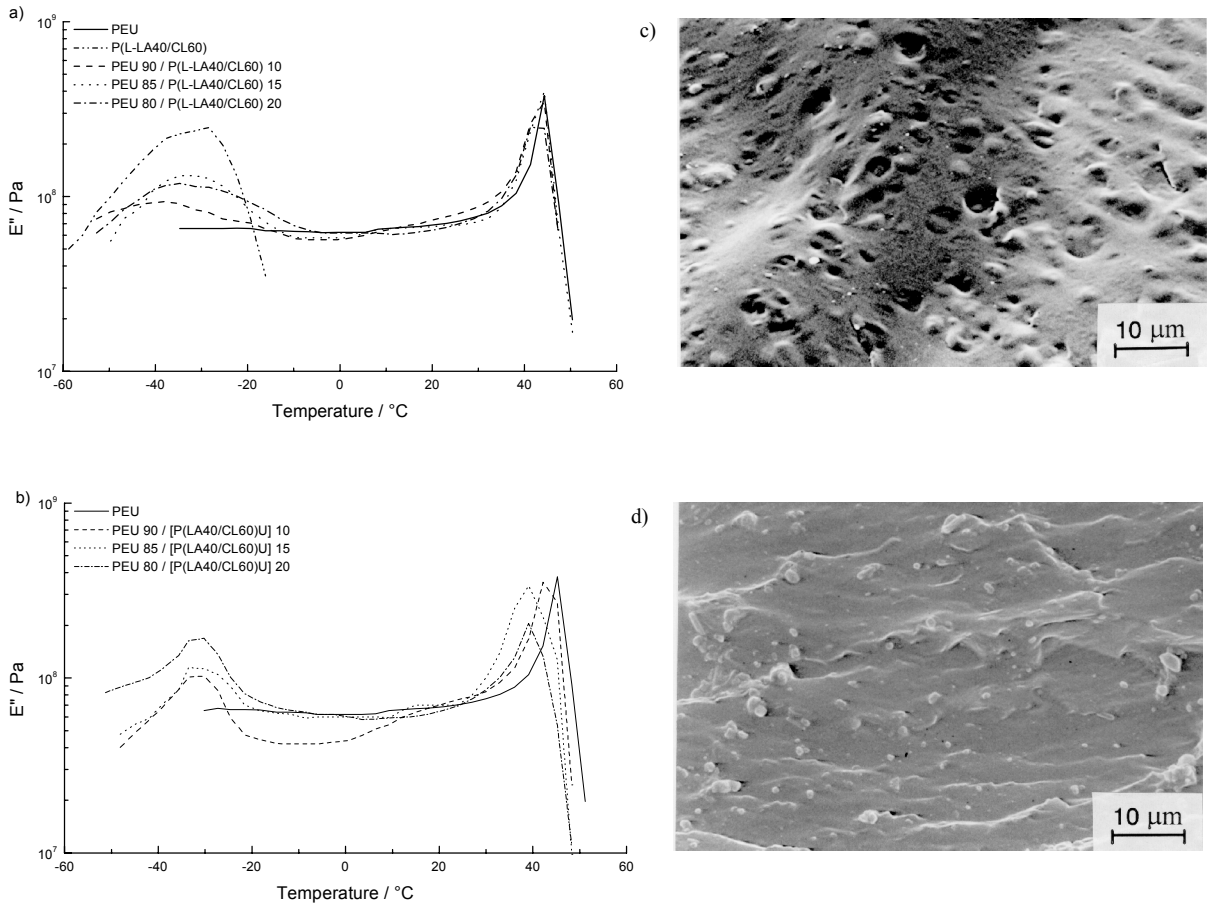

Figure 12. Loss modulus (E") in DMTA curves as a function of temperature for a) PEU/P(L-LA40/CL60) and b) PEU/P(LA40/CL60)U blends. SEM micrographs of corresponding blends: c) PEU85/P(L-LA40/CL60)15 and d) PEU85/[P(LA40/CL60)U]15. (III)

Both P(L-LA/CL) and P(LA/CL)U elastomers made poly(ester-urethane) more ductile, and significant improvements to impact strengths were achieved. Whereas the initial impact strength of linear PEU was 7 kJ/m^2, the impact strength of the PEU80/P(L-LA40/CL60)20 blend was 28 kJ/m^2 and that for the PEU blend with 20 wt.% P(LA40/CL60)U elastomer as good as 43 kJ/m^2. However, adding 10 wt.% of P(L-LA/CL) increased the impact strength to 23 kJ/m^2, whereas

adding the same 10 wt.% of P(LA/CL)U only improved the impact strength slightly, to 13 kJ/m^2. This is attributed to better miscibility of P(LA/CL)U with poly(ester-urethane).

3.3.1.2 Rubber composition

Rubber toughening is achieved by phase separation, which yields discrete rubber particles dispersed in a continuous matrix phase. Solubility between the matrix and the rubber, which can be evaluated by the difference in their solubility parameters, influences the phase separation and interfacial adhesion. According to the calculations, through the use of group molar attraction constants,[137] increasing the amount of ε-caprolactone in the elastomers decreases the solubility parameter and increases the probability of phase separation. The calculations predict that poly(ester-urethane) should be immiscible with poly(L-lactic acid-co-ε-caprolactone-urethane) elastomer that contains about 40 to 100 mol% of ε-caprolactone.

DMTA of the blends of PEU with P(LA50/CL50)U and P(LA30/CL70)U elastomers exhibited separated T_gs for rubber and matrix, indicating phase separation. Similarly, in PEU/P(L-LA35/CL65) blends, two separate glass transitions were found. PEU/P(L-LA54/CL46) blends showed the T_g of the PEU phase, which had shifted somewhat, and in just a few cases the rubber induced a very low peak. Rubbery copolymer particles were seen in SEM micrographs, though they were smaller than in PEU/P(L-LA35/CL65) blends. In contrast, the P(LA70/CL30)U elastomer was at least partly miscible with PEU. Only a very small peak at about 11EC was seen for the blend with rubber contents of 20 and 30 wt.%. SEM analysis also revealed this miscibility, without any clearly dispersed rubber particles. According to both DMTA and SEM, the PEU/P(L-LA76/CL24) blends were miscible.

As expected from the similarities in the chemical nature of blend components, interaction was also observed at the rubber-matrix interface. Partial mixing of the rubber and matrix phases causes the secondary loss peak to move upwards and the primary loss peak to move downwards in the temperature scale. The T_gs of the PEU matrix and P(LA/CL)U rubber moved slightly towards each other. In the blend of linear PEU and P(LA30/CL70)U, for example, T_g of the rubber increased from -46 to -45 °C, while the T_g of PEU decreased from 43 to 40 °C with increasing rubber content from 10 to 30 wt.%.

As a general pattern in mechanical properties, addition of the rubber increased the impact strength markedly, in particular at higher rubber loadings. The toughening effect of various rubbers in heterophase blends, i.e., P(LA50/CL50)U, P(LA46/CL54)U, P(LA30/CL70)U, P(L-LA35/CL65), and P(L-LA54/CL46) rubbers, were about the same, denoting the formation of a heterophase structure as a key parameter in rubber-modification. In partially miscible blends, improvements in impact strength were not achieved; P(LA70/CL30)U softened the PEU. Typically for rubber-modification, tensile modulus and strength showed a downward trend as a function of rubber concentration but remained at an acceptable level.

3.3.1.3 Degree of functionalization and crosslinking of rubber

Degree of crosslinking and melt viscosity of the rubber are important parameters to produce optimum particle dispersion for high impact modification. A series of studies was carried out to investigate the influence of the diisocyanate end-functionalization, and accomplished crosslinking of the P(LA30/CL70)U rubber on morphology and mechanical properties of the blends. The polymerization of the elastomer was interrupted when it still had reactive end-groups capable of interfacial reactions with the matrix. Left at room temperature, the reactions in the elastomer continue and the degree of crosslinking increases, as seen in Figure 13. The elastomer samples 1, 3, 5, 7, and 9 (number refers to reaction time in days) were blended with the PEU matrix after these predetermined reaction times and, after blending, all blends were characterized concurrently.

As found in publication IV for this elastomer and compositions, the best degree of crosslinking, i.e. gel content, was about 5 wt.%. A higher degree of crosslinking was associated with poor values of impact strength. SEM revealed that degree of crosslinking in the rubber also has a marked effect on the blend morphology (Figure 13). The morphology changed dramatically with increasing degree of crosslinking in the rubber. In the uncrosslinked elastomer (sample 1 in Figure 13), particles broke down into small streak-like fragments, whereas with the highly crosslinked rubber (sample 9), the blend exhibited a structure with large, irregular globules of rubber. In the rubber-modified blend, which had the best mechanical properties, the morphology was intermediate. The impact strength of blend 5 was 54 kJ/m^2, whereas samples 1 and 9 had only 20 and 16 kJ/m^2, respectively.

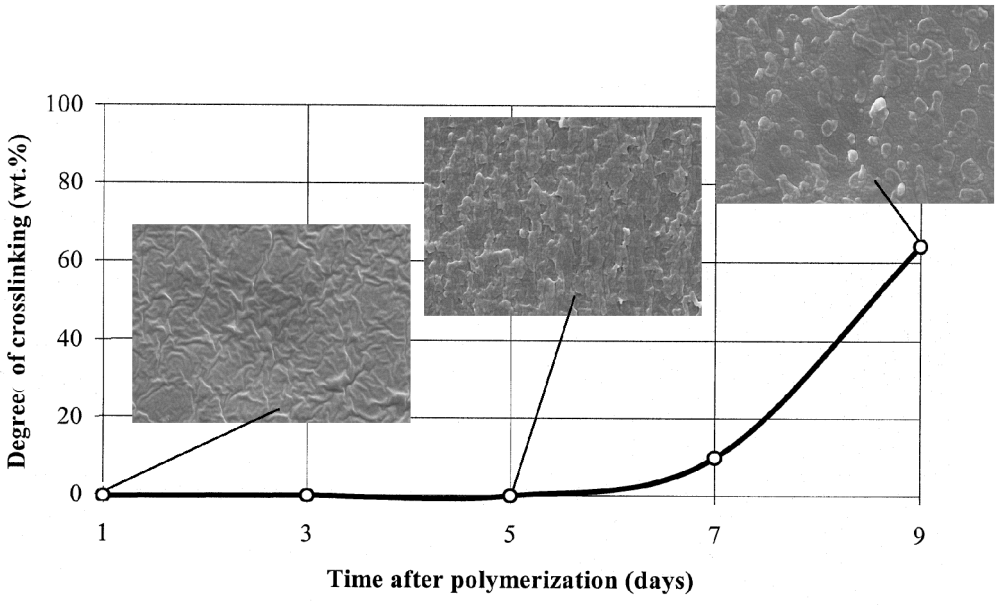

Figure 13. Effect of crosslinking of the elastomer on the morphology of PEU85/[P(LA30/CL70)U]15 blend.(IV)

The amount of reactive groups in the rubbers decreased with reaction time (i.e., time before blends were made), which is assumed to decrease interactions at the rubber-matrix interface. The T_g of the matrix moved less toward the T_g of the rubber as the reaction time of the rubber was increased, which shows that the partial miscibility at the interface was weakened. As mentioned however, in this series, the best impact values were achieved with the elastomer that was allowed to react for 5 days. Evidently, in these blends, the degree of crosslinking of the rubber is more important for impact strength than are interfacial reactions.

3.3.1.4 Type of matrix polymer

In these rubber-modification studies, two different, linear and branched poly(ester-urethanes) were used. As described earlier, the modification was made by changing the amount of HMDI in chain linking polymerization. In blends of branched PEU, more interactions between matrix and rubber were found compared to the linear form. The T_g of matrix in branched PEU blends was mostly at a slightly lower level from the initial value. Corresponding small differences were also noticed in T_g of the rubber phase. In PEU/P(LA50/CL50)U and PEU/P(LA30/CL70)U blends, SEM analysis revealed round dispersed rubber particles with linear PEU, but island-like areas with branched PEU. The tensile properties of the blends obtained from linear and branched PEU were closely similar. As a general difference with P(LA50/CL50)U and P(LA30/CL70)U, the rubbers softened branched PEU more than linear PEU, indicating less improvement in impact strength but greater increase in strain.

3.3.2 Enhancing properties with fillers

Blending of PEU with fillers was reported in publication V, where organic and inorganic fillers were studied as reinforcing agents. Improvements in both mechanical and thermal properties were obtained. The addition of particulate or fibrous filler increased the stiffness almost linearly with filler content. Improvements in tensile strength were also achieved. As expected, glass fibre reinforcement gave the highest strength value, 75 MPa, and wollastonite with high aspect ratio up to 57 MPa, compared to PEU's initial value of 46 MPa. Aktisil and talc showed somewhat lower values than neat poly(ester-urethane), but again strength increased with the filler content. A slight decrease in tensile strength at higher filler loading was observed only with flax fibre, which was attributed to the higher volume fraction than for the other fillers.

Enhancements of impact strength were obtained with particulate mineral fillers and, generally, only small reductions were seen in other PEU/filler blends. Significant improvement in impact strength was achieved with wollastonite: 15 wt.% of wollastonite increased the impact strength to 23 kJ/m^2, which is a level of practical importance. The effect of the aspect ratio of wollastonite is depicted in Figure 14. With a ratio of 8:1 (L:D), tensile modulus and impact strength increased, whereas wollastonite (FW325) with an aspect ratio of 3:1 showed only a slight increase

in modulus and a decrease in both tensile and impact strength. Wollastonite without surface treatment (WIC 10) had somewhat lower values than the surface-treated with aminosilane, although they showed the same trend in properties concerned.

The glass transition temperature of the PEU increased in the presence of filler. A marked 10°C increase in the T_g of PEU occurred with 15 wt.% wollastonite, talc, and glass fibre, and values 1-5°C higher than initial PEU were measured for blends with Aktisil, wood, and flax fibre. The stiffening effect induced by fillers reduces the matrix mobility and causes an increase in glass transition temperature.

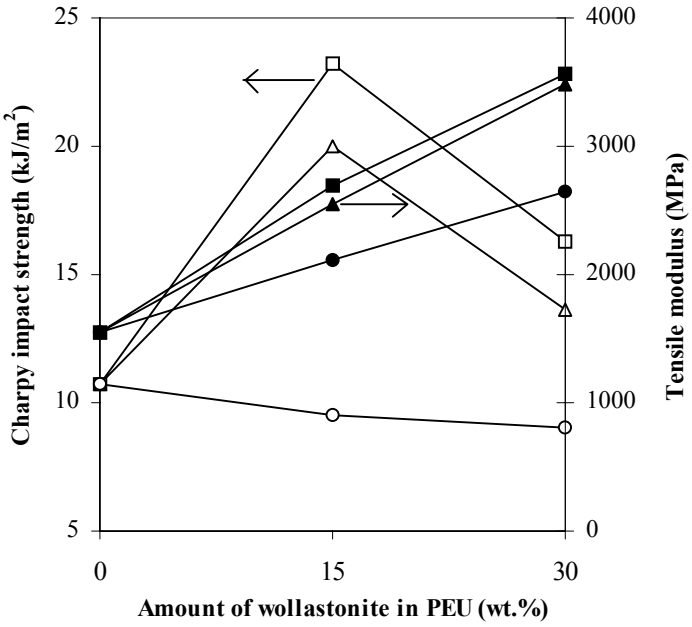

Figure 14. Effect of aspect ratio and surface treatment on the impact strength (open symbols) and tensile modulus (solid symbols) of poly(ester-urethane)/wollastonite blend: (□) WIC10PA (L/D 8:1, surface treatment), (Î) WIC10 (L/D 8:1), (○) FW325 (L/D 3:1).(V)

3.3.3 Ternary composites

Inspired by earlier study in our laboratory, rubber-modifications and a study concerning reinforcement with fillers by Hiljanen-Vainio et al.[103], ternary phase polymer composites containing soft elastomer and rigid filler became of interest in achieving an optimum balance of impact strength and stiffness.

Although all rubber-modified formulations displayed a reduction in tensile modulus as elastomer content increased, the modulus values with 15 wt.% filler addition were all higher than those for neat PEU, even at high rubber loadings, as seen in Figure 15a for wollastonite. At 30 wt.% filler addition the stiffness increased even as much as twofold. Similarly, tensile strength decreased as a function of rubber content, and in the same way as for the PEU/elastomer binary

blends, though it was still relatively high. Tensile strengths were very high for glass fibre composite (48-75 MPa), as well as for PEU/elastomer/wollastonite compositions (35-57 MPa).

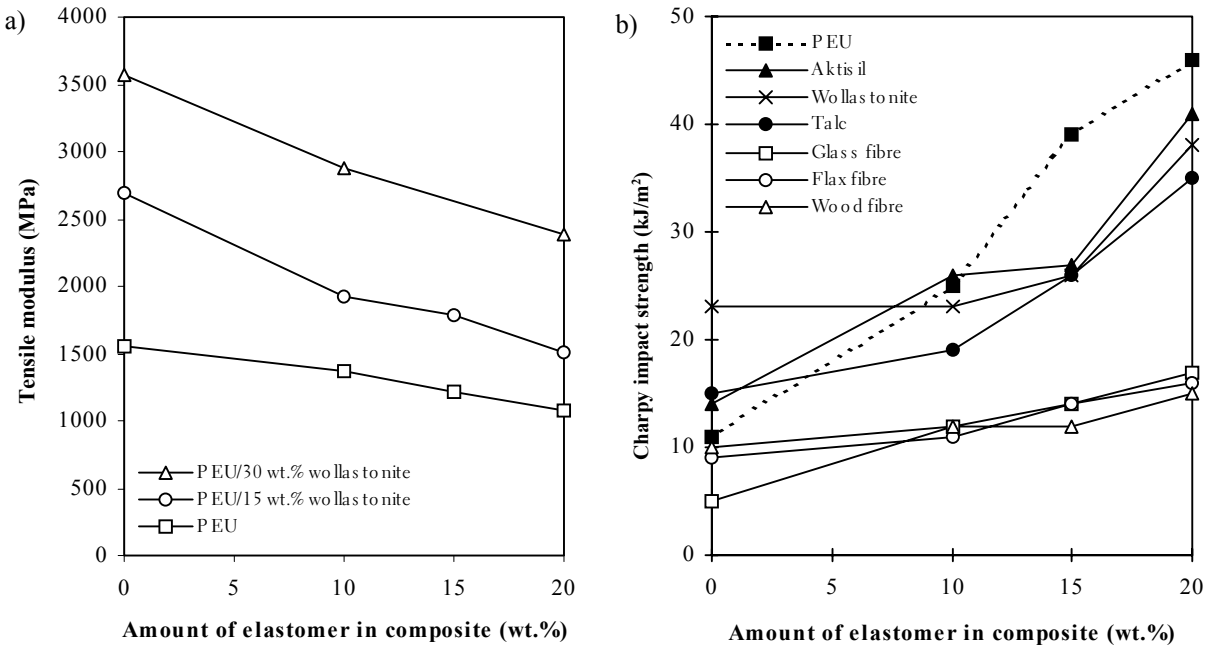

Figure 15. a) Tensile modulus of ternary poly(ester-urethane)/elastomer/wollastonite composites. b) Impact strength of ternary poly(ester-urethane)/elastomer/filler composites with 15 wt.% filler.(data from publication V)

In all blends, the impact strength increased with rubber addition (Figure 15b). Roughly two levels of toughness can be discerned. Composites with particulate fillers (i.e., wollastonite, Aktisil, and talc) showed excellent impact strength, although still slightly lower than that of rubber-modified PEU. The binary blend with 20 wt.% rubber had an impact strength of 46 kJ/m^2, whereas corresponding composites with 15 wt.% fillers were in the range of 35-41 kJ/m^2. The rubber toughening was less effective in constrained composites, i.e., in composites with fibrous fillers, with high filler loadings, or alternatively with organic fillers where the volume fraction was increased. Nevertheless, comparison of the mechanical properties of neat PEU and compositions containing both filler and elastomer, indicates that the addition of one component eliminates the decrease caused by another, and thus improves the balance of properties.

In multicomponent blends, the T_g values of the elastomer were somewhat higher than in binary blends of PEU/elastomer. This suggests that at least part of the elastomer is around the filler, causing this shift to higher temperatures by restraining molecular motions. According to SEM analysis, the elastomer was predominantly in the matrix phase in the form of finely dispersed particles (diameter - 0.1-1μm) and encapsulation of the fillers by the elastomer was not observed. The increase in T_g of PEU that was achieved with some fillers was shifted back to the initial temperature by the addition of elastomer phase in these ternary composites.

4 CONCLUSIONS

Knowledge of the structure-property relationships is of primary importance in order to be able to improve the properties of polymers. Poly(lactic acids) reflect a large family of polymers whose properties are varied by many factors, such as polymerization method and chirality of monomer. The previous studies of poly(ester-urethanes) in our laboratory have shown that chain linking of lactic acid oligomers is a highly efficient route for converting lactic acid to high molecular weight, biodegradable polymer. In the present work, it was shown that it also offers excellent possibilities for structural modification. By chain linking, together with a proper manipulation of readily available tools, copolymerization and blending, valuable materials with a broad range of properties can be produced. A chain linking method based on two reactive chain extenders, which take advantage of both reactive groups of the lactic acid oligomer, opens opportunities for both production development and structure modification. New types of polyurethanes, and polyurethanes with advantageous thermal properties, based on the copolymerization of lactic acid and ε-caprolactone or DL-mandelic acid, have been produced. In PEU blends, diversity of structure units and functional groups of poly(ester-urethanes) enables good adhesion between blend components. As a consequence of this work, several patents have been filed, concerning these novel materials and methods developed.[138,139,140]

The heat resistance of poly(ester-urethane) was improved by the copolymerization of lactic acid with DL-mandelic acid. This broadening of the operating temperature range is of clear practical importance. The incorporation of various comonomers, which impede rotation and stiffen the chain, clearly cause a large increase in T_g, whilst the same comonomers depress the rate of polycondensation. These problems associated with polycondensation and high acid values can be overcome by using a novel polymerization method for lactic acid oligomers based on two chain linking agents, first introduced in publication VII of this thesis. It was shown that the addition of 2,2'-bis(2-oxazoline) as a chain coupling agent during the final steps of melt polycondensation of polyester allows the production of higher molecular weight hydroxyl-terminated prepolymers without the use of diol compound. The obtained prepolymers, having very low acid values, are advantageous in diisocyanate linking for producing high molecular weight PLA. The use of BOX-HMDI combination polymerization also makes possible the use of high molecular weight prepolymers (M_w up to 72 000 g/mol), which were previously obtained with various catalyst-diol combinations.[136] In addition, BOX was found to have a beneficial impact on thermal stability.

The rheological properties of PEU were enhanced by modification of the structure of the polymer chains. An increase in the amount of chain extender (HMDI) caused branching, which was observed as broadened MWD and increased shear thinning at low frequencies. This is advantageous in the extrusion coating of paper, which is an attractive application for mass-volume biodegradable polymers. The use of branched PEU grades in extrusion coating would provide decreased neck-in even at high draw-down.

A new type of biodegradable polyurethane elastomer, based on random copolymers of lactic acid and ε-caprolactone has been polymerized by polycondensation followed by diisocyanate linking, and characterized with respect to structure and thermal and mechanical properties. The

properties of thermoplastic poly(L-lactic acid-co-ε-caprolactone-urethanes) changed with the molar ratio of the monomers in the copolymer. Small amounts of ε-caprolactone increased the strain of PEU, and at higher CL content the poly(ester-urethanes) exhibited elastomeric properties, having lower strength but significant elongation.

These elastomers were used in rubber-toughened blends, which were studied to overcome PEUs inherent brittleness. The toughening was achieved with finely dispersed poly(L-lactic acid-co-ε-caprolactone-urethane) and also copoly(L-lactide/ε-caprolactone) elastomer phase in the PEU matrix, and good compatibility between the two polymers. With P(LA/CL)U elastomer, interactions at the rubber-matrix interface were observed. The relationship between phase separation and mechanical properties of poly(ester-urethane) blends has been described. Significant improvements in the impact strength were achieved with the addition of rubber, particularly at higher rubber loadings. Tensile modulus and strength showed a downward trend as a function of rubber concentration but remained at an acceptable level. The comonomer composition of the rubber was found to influence the formation of heterophase structure: Increasing the amount of ε-caprolactone in the elastomer increased the phase separation. The solubility parameter calculations, that predict blend components to be immiscible when the P(LA/CL)U elastomer contains about 40 to 100 mol% of CL, were in very good agreement with experimental results. Thus, the toughening effect of P(LA50/CL50)U and P(LA30/CL70)U rubbers was about the same, whereas P(LA70/CL30)U softened the PEU, causing greater lowering of tensile modulus and strength. Furthermore, the degree of crosslinking in the P(LA/CL)U rubber was an important factor in the impact modification.

In mass volume applications, the cost-effectiveness of the biodegradable polymer is important. Chain extension reactions have been found to be an economically feasible route for the preparation of lactic acid polymers, and the addition of fillers will further lower the cost of the material. In addition, fillers in the polymer matrix improve thermal and mechanical properties. Various organic and inorganic fillers increase the stiffness of PEU almost linearly with filler content. A unique feature was that 15 wt.% wollastonite increased the impact strength to a level of practical importance. Concerning the temperature use range, a marked 10°C increase in T_g of PEU was achieved with some fillers.

There are two adverse effects in PEU blends: addition of high modulus filler to a matrix results in increased brittleness and an increment in the toughness of rubber blends is obtained at the expense of their stiffness and strength. Therefore, novel poly(ester-urethane) composites containing a combination of rubbery and rigid dispersion phases were prepared. The best improvements in ternary composites were obtained with particulate mineral fillers. Results showed that useful composites with an excellent balance of properties can be successfully developed by exploiting rubber-modification and the reinforcing effect of a filler.

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